WORKS BY WILLIAM T. HALL

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Analytical Chemistry

BASED ON THE TEXT OF

F. P. TREADWELL

Late Professor of Analytical Chemistry at the Polytechnic Institute of Zurich

TRANSLATED, ENLARGED AND REVISED

BY

WILLIAM T. HALL

Associate Professor of Analytical Chemistry, Massachusetts Institute of Technology

VOLUME II
QUANTITATIVE ANALYSIS

EIGHTH EDITION

REWRITTEN AND RESET

TOTAL ISSUE FORTY-SEVEN THOUSAND

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PREFACE TO THE EIGHTH ENGLISH EDITION

So many changes were made in the text that it was found best to ı the entire book. Much valuable help was obtained from Dr. W. R. Schoeller of London, England, who examined the entire book critically and suggested many changes as a result of his extensive laboratory experience. Dr. Schoeller suggested dropping some of the older procedures, which has been done, and also offered some well-tested methods for determining columbium, tantalum and certain other elements. The "Outline of a Course of Instruction" which was introduced into the previous edition has been dropped because the work given to students in chemical engineering at the Massachusetts Institute of Technology has now been printed in a smaller text on Quantitative Analysis. Mr. Charles H. Ross assisted in reading the proofs.

W. T. H.

May, 1935.

PREFACE TO THE SIXTH ENGLISH EDITION

F. P. Treadwell was born in New Hampshire in 1857. He completed his education in Germany, receiving the Ph.D. degree at Heidelberg. In 1878 he became assistant to Bunsen but left him in 1883 to work under Victor Meyer. In 1894 he was made Professor of Analytical Chemistry at Zurich where he remained until his death in 1918.

Twenty years have elapsed since the second volume of the English edition of this book appeared. Numerous changes have been made from time to time but now for the first time the text has undergone a complete revision. Hardly a page has remained unaltered.

In the main the methods are the same as those described in the tenth edition of the German text but at least twenty per cent of the book is unlike the German text. The aim has been to make the methods conform to the best American practice. Particularly with regard to standards of mass and volume has this been true. As far as possible the work at the German testing bureaus has been replaced by results published by the Bureau of Standards at Washington. This attempt to follow the Bureau of Standards has even led to the adoption of the *milliliter* instead of *cubic centimeter*. This change has been adopted by the principal instrument makers of the United States although not sanctioned by the editors of our chemical journals. Most burets, pipets and measuring cylinders are now marked in milliliters and it seems irrational to tell a student that *ml* means *cc.* It is of course more practical to define the liter as the volume occupied by one kilogram of water under certain conditions than it is to attempt to measure the volume in cubic centimeters. It is estimated, however, that the liter represents 1000.027 cubic centimeters or one drop of water more than the theoretical value. Since this is about as close as the volume can be read in an ordinary measuring-flask it is easy to see why most chemists prefer to use *cc* instead of *ml* since all the other nations of the world are doing it.

Before the publishers agreed to publish an English edition of this book in 1902, the opinion of several well-known chemists was asked. One of the strongest letters in praise of the Treadwell book was written at that time by Dr. W. F. Hillebrand, who knew Treadwell personally. At Dr. Hillebrand's suggestion, again, Dr. G. E. F. Lundell has now carefully read the entire text of the fifth edition and has offered more

than one hundred suggestions based, for the most part, on his experienc as an analyst at the Bureau of Standards. Dr. Lundell has also fur nished directions for a number of new methods and for some old one that have been altered at the Bureau.

Besides this painstaking work of Dr. Lundell, the entire proof has been read by S. G. Simpson, C. E. Carlson and A. F. Kaupe, all graduates of the Massachusetts Institute of Technology.

Owing to an unexpected demand for the book during the last few months, it has been necessary to rush the book through the press in about one-half the time that had been planned. Probably some typographical errors have escaped correction. The editor will be grateful to have such errors pointed out, and any suggestions with regard to possible improvements will be welcomed.

WILLIAM T. HALL.

MASSACHUSETTS INSTITUTE OF TECHNOLOGY,
February, 1924.

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QUANTITATIVE ANALYSIS

INTRODUCTION

The purpose of a quantitative analysis is to determine the relative quantity of one or more constituents of a compound or of a mixture. The methods to be employed depend somewhat upon the nature of the substances to be determined so that, as a rule, a qualitative analysis should precede the quantitative one. The chemical reactions used in quantitative analysis are, for the most part, reactions which are used or can be used as qualitative tests, and the chemical principles involved are the same. In quantitative analysis, however, it is necessary to measure accurately the quantity of sample taken and either the quantity of reagent required to cause a definite reaction to take place or the quantity of one of the products formed by the reaction. Quantitative analysis, therefore, differs from qualitative analysis with respect to the necessity of making careful measurements of materials. Since all chemical research is based upon quantitative analysis, it is clear that the ability to make accurate analyses is one of the most important assets of the chemist irrespective of the field in which he may choose to work eventually.

The most important tool of the chemist is the balance by which weighings are made.* The balance used by the chemist combines the physical principles of the lever and the pendulum (Fig. 1.)† The *beam*, from which the *scale pans* are suspended, represents a horizontal lever with two arms of equal length. To be serviceable, a balance must be *accurate* and *sensitive*. It fulfills the first condition if (1) the arms are actually of equal length, (2) the point of support (the fulcrum about which the beam rotates) lies above the center of gravity, and (3) the fulcrum (center

* Strictly speaking, the balance determines masses and not weights. The unit of *mass* is the *gram* and the unit of *weight* is the *dyne* in the absolute system. The mass in grams multiplied by the acceleration of a falling body due to gravity, gives the weight in dynes. At any given place, therefore, the weights are proportional to the masses so that it is common practice to neglect the value of gravity and speak of a *weight* of so many grams. The masses determined by the chemical balance are independent of the value of gravity whereas a spring balance may not show the same weights for the same masses at different places on the earth's surface.

† Reproduced, by permission, from Catalog No. 8 of Christian Becker, Inc.

knife-edge) and the knife-edges from which the pans are suspended lie in the same plane and are parallel to one another.

The beam of the balance is provided with a long pointer which swings over a fixed scale near the base of the balance case. A small adjustable nut on the pointer, sometimes above and sometimes below the beam, serves to raise or lower the center of gravity of the moving parts and

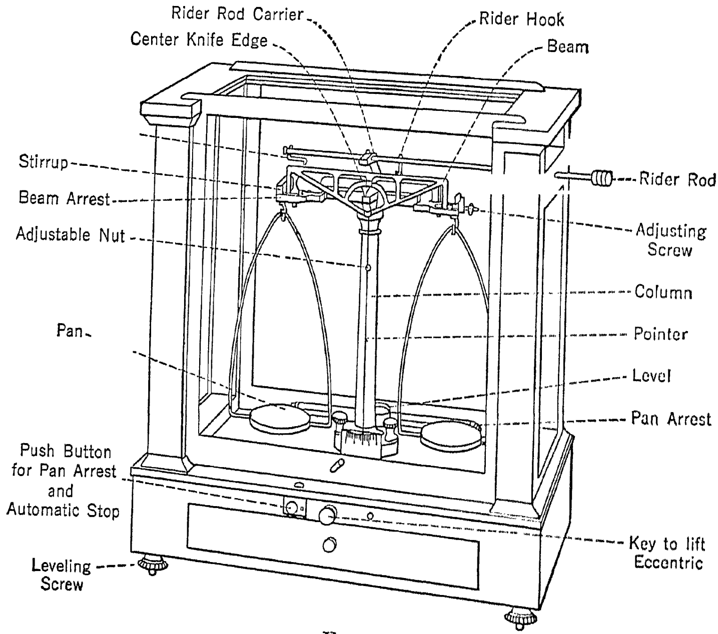

FIG. 1.

ou
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t the middle of the bea
ally made of polished ag
edge rests upon a plate of
with very little friction. At
from which the balance pans are
beam should be raised so that the
their bearings. This is effect
key at the front of the balance
wise, the beam is raised. With
resting on the

edge which is
is in use, this knife-
the beam can swing
are other knife-edges
When not in use, the
are not in contact with
means of a frame operated by a
By turning the milled head
the

and should finally come to rest at the zero-mark. If a small weight is added to either pan the beam and the pointer will swing through an angle and take up a new position of equilibrium. This new position will be the result of the moments of three effective forces — the weight of the beam and the weights in each pan.

The angle α which the pointer at its new resting place makes with its original position is determined by the excess weight, p, the length of the balance arm, l, the weight of the beam, q, and the distance, d, between the center of gravity and the point of support of the beam. Expressed mathematically,

$$\tan \alpha = \frac{p \cdot l}{q \cdot d}$$

The *sensitiveness*, or *sensibility*, is measured by the angle α when p has a definite weight, usually 1 mg. Since the tangent of a small angle is practically the same as the angle, and the tangents of the angles that the pointer makes are directly proportional to the number of divisions between the two points of rest on the scales, it is customary to regard the sensitiveness or sensibility as *the number of scale divisions that the zero-point is displaced by an excess weight of 1 mg.*

It follows, then, that the sensitiveness of a balance is directly proportional to the length of the balance arms and inversely proportional to the weight of the beam and to the distance of the center of gravity below the point of support. It is clear also that the observed deflection is proportional to the length of the pointer.

The conditions for maximum sensitiveness are more or less conflicting. Thus long arms are incompatible with minimum weight. The length of arms is also limited by the fact that the longer the arms are, the greater the time required for one complete swing of the pointer. The weight of the beam also affects the time of swing in the same manner. On the other hand it is important that the beam should be rigid.

Long arm balances, although sensitive, possess the disadvantage of a long time of swing which renders weighing a tedious process. For moderate loads, short arm balances with light beams of aluminum alloy are sensitive and fast.

It is possible to decrease the time of swing by lowering the center of gravity, but this makes the balance less sensitive. For ordinary work, it is well to adjust the sensitiveness so that 1 mg. excess weight will displace the zero-point at least five scale divisions with light loads. The center of gravity must always be below the knife-edge or the balance will be in neutral or unstable equilibrium.

Precautions in the Use of a Balance

1. The balance should rest upon a firm support which is practically free from mechanical vibration. Direct sunlight should not fall upon the balance as it will cause irregularities and errors in weighing.

2. When not in use the balance beam should always be raised off the knife-edges as otherwise these are likely to be injured by jarring.

3. The beam should always be lowered slowly and carefully.

4. The beam should never rest upon the knife-edge while weights or substances are being added to or removed from the pans.

5. The beam may be set swinging by dropping the rider upon the beam or removing it for a moment. It may also be set in motion by fanning one pan gently with a motion of the hand, but in no case should motion be started by touching the pan or by suddenly lowering the beam upon its knife-edge.

6. All weighings should be made methodically, trying the weights one after another in their proper order.

7. Before making a weight, the adjustment should always be tested. The balance is properly adjusted (*a*) when it is level, (*b*) when the pointer rests at the zero-mark with the beam raised, (*c*) the pointer should swing equal distances on either side of the zero when the beam is set in motion with no load in the pans.* If the balance has pan arrests which work independently of the mechanism that lowers the beam, these arrests should be adjusted so that the pointer is at the zero-mark when the beam is on its knife-edge and the pan arrests are in place.

8. Final adjustment with the rider and all observations regarding the swing of the pointer should be made with the balance case closed to prevent errors arising from air currents. On leaving the balance, the case should always be closed.

9. The weight of a substance should be recorded, *first*, by adding up the weights missing from the box (in which every weight should always have its own place), and *second*, by adding up the weights that are on the pan. After the final weight has been made, it is convenient to make this second addition when the weights are being returned to the box. By always checking the weights as a matter of habit, serious errors are often avoided.

10. Substances to be analyzed should never be placed directly upon the balance pan but on a watch glass or in a tube. The object should not be warmer or colder than the air in the balance case. Air currents

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* Some workers prefer to adjust the balance so that the pointer rests three or four divisions to the right with no load in either pan. Cf. Brinton, *J. Am. Chem. Soc.*, **41**, 1151 (1919).

from a hot body make it weigh too light and condensation of moisture on a cold body makes it appear too heavy.

11. Care should be taken not to overload the balance.

A separate set of weights should be provided with each balance. In analyzing a given material, the chemist is required to determine the weight ratios of the various constituents. He reports the per cent of iron present rather than the weight. It is important, therefore, that the weights in any set should stand in the proper relation to one another and relatively unimportant whether the 10-g corresponds exactly to the 10-g weight in some other set. In analyzing ores for precious metals, it is customary to weigh out a large sample on a "pulp balance" which need not be sensitive to 1 mg. The analysis is finished by weighing a very small fragment of metal on a "button balance" sensitive to 1/100 mg. Ordinarily, however, all of the weighings used in any chemical analysis should be made with the same balance and the same set of weights. If a weight is lost or misplaced, a new weight should always be tested to see if it bears the proper relation to the other pieces in the set.

Sets of weights used in chemical analysis usually contain a 50-g weight and sometimes a 100-g weight. Sometimes the smallest weight is 1 mg, but a set need not contain any weight smaller than 10 mg. The numbers on the weights indicate grams when the value is 1 g or over and milligrams if the weight is a fraction of a gram.

Weights smaller than 10 mg are usually obtained by the use of a "rider" or small piece of aluminum wire which may be shifted to various positions on the beam of the balance. The manner in which the beam is divided varies with balances of different makes. When the rider is placed directly over the knife-edge that supports the right pan, it indicates its true weight; and when it is placed at a fraction of the distance between middle and outer knife-edges, it indicates that fraction of its true weight. Riders as a rule weigh 5, 6, 10, or 12 mg. Balances which are made so that the rider can be placed directly over the pan suspension usually take a 10-mg rider or a 5-mg rider. Balances which are made with the top of the beam rounded off at the ends usually take a 12- or 6-mg rider. The larger divisions on the beam graduations are always 1 mg apart when the proper rider is used. The smaller subdivisions are either tenths or fifths of a milligram.

The *chainomatic balance* (Fig. 2) does not require a separate rider. One end of a small gold chain is fastened to the balance beam and the other end to a hook which can be moved up and down a vertical scale. This hook is operated by a milled head outside the balance case on the right. Movement of the hook changes the weight of chain that is sup-

ported by the beam so that the positions on the scale correspond to milligrams. This may be adjusted while the balance is in motion.

Methods of Weighing

It is important to keep the pans, beam, bearings and all parts of the case clean and free from dust and chemicals. Before starting to weigh, see that the balance is properly adjusted, determine the *zero-point* and the *sensibility* or *sensitiveness*. If necessary, turn the leveling screws at the base of the case until the spirit level back of the pillar shows the correct position. Note also whether the knife-edges are in the proper positions with respect to the bearings and whether the pointer rests at the zero-point of the scale. Lower the beam rest, by slowly turning the knurled knob at the bottom of the case in an anti-clockwise direction,* and see that the pointer is still at the zero-point when the pans are resting on the pan rests, making the proper adjustments, if necessary. Then with the balance case closed, release the pan rests and see that the pointer is quiet or moves back and forth to equal distances on both sides of the zero-mark. If necessary, move the adjustment screw on the end of the beam, but it is better to allow for a slight zero error, when it is not more than one scale division, than to make frequent adjustments.

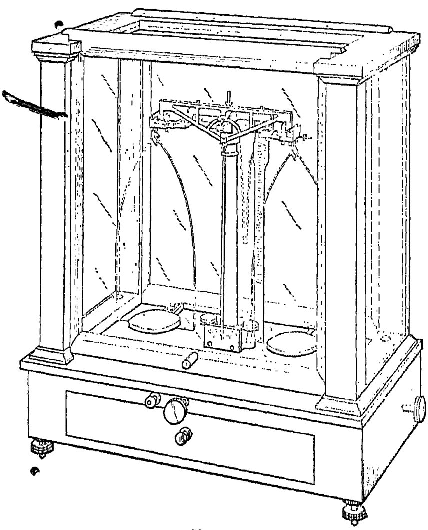

Fig. 2.

The pointer swings as a pendulum and, owing to air resistance, is subject to a damping, or shortening of the swing, and unless the eye is exactly in alignment, there is a parallax error in reading the position of the pointer on the scale. The half-way point is best determined by taking the half-way point of two or more complete swings. A complete swing of a pendulum involves a return to the starting place, and the measurements will represent complete swings if the final reading is

* In putting anything on the balance pan or taking anything off, the balance beam should always be supported and not resting on the central knife-edge.

taken on the same side as the initial reading so that there will be one more reading on one side than the other (see *Weighing by Swings*). If the center knife-edge is sharp so that there is little friction to overcome save that of the air, the damping will be slight, and negligible if the swing is made short; therefore for ordinary work it is sufficient to take the half-way point of a half-swing, with each turning point less than five scale divisions from the zero-mark. With these short swings, moreover, there is less danger of parallax errors than with long swings.

After taking the zero-reading, the next thing is to determine the sensibility or *number of scale divisions that the zero-point is displaced by a load of 1 mg*. The sensibility varies with the load,* but it is well to know how sensitive the balance is at the start because this knowledge will help the operator to make rapid weighings.

Rapid Method. — For ordinary work, it is convenient to adjust the center of gravity by means of the adjusting nut on the pointer, so that a load of 1 mg. will make the pointer have an initial swing of at least five scale divisions to the left when the pan rests are carefully released. In weighing, note the initial swing when the rider indicates within 0.5 mg of the correct weight. Then change the position of the rider so that the initial swing is a little to the other side of the zero-line and note the new swing; from these two readings estimate where the rider should be to give no swing. This method of making two trials one on each side of the true weight is more rapid and more accurate than attempting to place the rider where the swings will be exactly the same as in making the zero-reading. For very precise work, however, weights should be made by the *method of swings*, and corrections should be made for balance arm error and for buoyancy due to air. The weights should be carefully calibrated.

Single Deflection Method. — Adjust the balance so that the pointer swings 3 or 4 divisions to the right when the pan support is released and rests on this side of the zero-reading on the scale. In weighing, add weights until this same deflection is obtained on releasing the pan support. This method of weighing is rapid but is inapplicable to a balance which has a single release operating both beam and pan supports.†

* This is because the center of gravity changes with the load. How this changes, depends upon whether the three bearings lie in the same plane or not. As a rule, the sensibility is lowered by increasing the load in the balance pans, partly because the beam becomes slightly distorted and the center of gravity is lowered, but if the three bearings are exactly in the same plane, and the beam is absolutely rigid, the center of gravity will rise, but never reach the level of the middle knife-edge, so that increasing the load will then increase the sensibility.

† Brinton, *J. Am. Chem. Soc.*, **41**, 1151 (1919).

Method of Swings. — First of all determine the zero-reading of the balance by setting the beam in motion (without any load in either pan), observing and recording the turning-points, or extreme positions, of the pointer on the scale of an even number of complete swings and take the mean of the readings. The first complete swing may be inaccurate on account of the jar in shutting the balance door, etc. Remember that a complete swing starts and ends on the same side, so that for an even number of complete swings an odd number of readings must be taken. In order to give the same algebraic sign to all the observed readings it is best to number the divisions on the scale from left to right from 0 to 20 so that the zero-point in case both balance arms were of equal length and weight would be numbered 10. It is to be noted that when the zero-reading (the point of the scale at which the pointer rests when the balance is in equilibrium with nothing in either scale pan) coincides with the zero of the scale, it may change during the course of the day, so that disregard of this fact may lead to a considerable error. The cause of the displacement of the zero-reading is that the first condition for the accuracy of a balance is not fulfilled. On account of unequal warming the arms become of unequal length.

The next thing to be determined is the sensitiveness of the balance for the object to be weighed. For this purpose place the object in the left balance pan and weights in the right pan until equilibrium is established as nearly as possible and determine the rest point of the

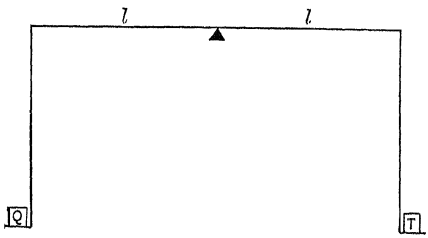

FIG. 3.

pointer on the scale in the same way that the zero-reading was made above. Add or remove an additional weight of 1 mg. by means of the rider, and determine the rest point again.

The difference (d) between this and the previous point of rest gives the sensitiveness of the balance. Assuming the zero-reading to lie at 10.22, the first rest, obtained with a load of 19.723 g, to be at 9.80, and the rest point with a load of 1 mg less (with a load of 19.722 g) to lie at 12.32, then the sensitiveness of the balance will amount to 12.32 − 9.80 = 2.52 scale divisions.

As the zero-reading of the balance was at 10.22 and the rest point with a load of 19.723 g was 9.80, it follows that the object was lighter than the weights in the right-hand pan, and in fact the excess of weights in the pan was sufficient to move the point of rest 10.22 − 9.80 = 0.42 of a division on the scale. This amount can be calculated from the determination of the sensitiveness of the balance as follows:

Since 2.52 of the scale divisions correspond to 1 mg, then 0.42 of a scale division corresponds to $\frac{0.42}{2.52} = 0.17$ mg, or about 0.2 mg.

The true weight of the body in air is consequently 19.723 − 0.0002 = 19.7228* g.

In making a weighing one should always accustom himself to note the observations methodically, as follows:

Assume that a platinum crucible is to be weighed.

Zero-Reading		I. Rest Point with Load of 12.052 g		II. Rest Point with Load of 12.053 g	
Left	Right	Left	Right	Left	Right
4.2 4.6 5.1	17.6 17.1	5.8 6.2 6.6	18.7 18.3	3.5 3.8 4.2	15.8 15.4 ....
Sum = 13.9 Mean = 4.63	34.7 17.35 4.63	18.6 6.2	37.0 18.5 6.2	11.5 3.83	31.2 15.60 3.83
Sum of both means = 21.98 Mean = 10.99		....	24.7 12.35	....	19.43 9.71

Sensitiveness = 12.35 − 9.71 = 2.64 scale divisions.
12.35 − 10.99 = 1.36 scale divisions.
1.36 : 2.64 = 0.5 mg.
Weight of crucible = 12.052 + 0.0005 = 12.0525 g.

The sensitiveness of a balance varies slightly with the load. It is simplest to determine once for all the sensitiveness for 50 g, 20 g, 10 g, 5 g, and 2 g, place a card in the balance with the results obtained, and use the numbers as required.

* As most analytical balances will scarcely detect with certainty less than $\frac{1}{10}$ mg, the weight is expressed only to the fourth decimal. If the fifth decimal place in a calculation amounts to five or more, the number in the fourth decimal place is increased one.

In this way the sensitiveness of a balance

with a load of	was found to equal the following number of scale divisions
50 g	2.23
20 "	2.28
10 "	2.64
5 "	2.66
2 "	2.66

The determination of the zero-reading, however, must be made with every weighing. If a number of weighings are to be made one after another it suffices to determine the zero-point at the beginning and at the end and to use the mean of the two determinations. With very heavy loads, however, the zero-reading should be determined before and after each weighing and the mean value used.

Balance-Arm Error

Both of the preceding methods of weighing are subject to a constant error if the lengths of the balance arms are not exactly the same. Such an error can be corrected by the following method of *indirect weighing*. The balance beam may be regarded as a lever with the fulcrum in the middle. In a lever, equilibrium results when the statical moments are equal. By *statical moment* is understood the product of the force and

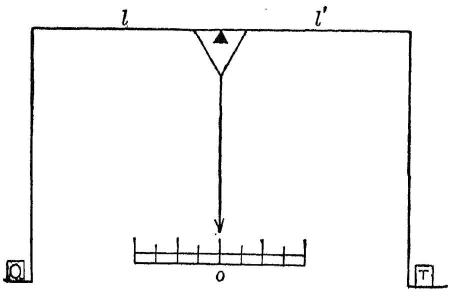

FIG. 4.

the length of the lever-arm, and the length of the lever-arm is the perpendicular distance from the axis of revolution (the fulcrum) to the line of action of the force.

Borda's Method of Weighing by Substitution

Place the object Q in the left pan and counterbalance or tare it by means of shot, sand, or weights. Then remove Q and establish equilib-

rium again by placing weights in its place. We have, then, as a result of the first weighing,

$$Ql = Tl_1$$

and from the second weighing,

$$Pl = Tl_1$$

from which it follows:

$$Ql = Pl$$

$$Q = P$$

This method is used chiefly in weighing large objects.

Ratio of Lengths of Balance Arms

In a perfect balance of the type used in the chemical laboratory, the two arms of the beam are equal. Most balances are not perfect and there is usually a slight difference in the lengths of the arms. If r is the length of the right arm and l that of the left arm, then the true weight, w_0, of an object is the apparent weight w_a, as obtained by weighing it in the usual manner, multiplied by the arm ratio.

$$w_0 = w_a \frac{r}{l}$$

If the true weight has been determined for an object of suitable size (such as that of about half the load which the balance is designed to bear) then the arm ratio $\frac{r}{l}$ can be determined from the above equation and used as a correction factor. The ratio should be expressed to the fifth decimal.

Double Weighing

Place the object Q on the left pan and balance it against weights on the right pan. When equilibrium is reached

$$Ql = W_1l'$$

when W_1 represents the weights used, l the length of the left balance arm, and l' the length of the right arm. Transfer the object to the right balance pan and balance it with weights on the left pan. Then, if W_2 represents the necessary weights,

$$Ql' = W_2l$$

Multiplying the first equation by the second one we get

$$Q^2ll' = W_1W_2ll' \quad \text{or} \quad Q^2 = W_1W_2 \quad \text{and} \quad Q = \sqrt{W_1W_2}$$

If the balance is perfect, W_1 will be the same as W_2 and with any good balance the difference between the two values will be small; in such cases the algebraic mean is practically the same as the geometric mean so that no sensible error is caused by assuming that the true weight is

$$\frac{W_1 + W_2}{2}$$

Reduction of Weighings to Vacuo

When a substance is immersed in water it experiences a buoyant or floating effect. Its true weight is diminished by the weight of water that it displaces. In exactly the same way, an object weighed in air against brass weights is buoyed up by the air that it displaces, but the weights are also subject to the same effect. If brass is weighed in air against brass weights, the buoyancy will be the same on both sides of the balance and the weight will be the same in a vacuum as in the air. If a material of lower density is weighed against brass, the weight in a vacuum will be greater than the apparent weight in air, and conversely if a denser material such as gold is weighed with brass weights, the weight in a vacuum will be smaller than the weight in air.

The degree of precision attainable in the buoyancy correction depends upon the precision with which the volumes and the density of air can be determined. In the case of the weights, several materials are used in the construction of every set, but since all weighings are made in the air and the values are obtained by comparison in the air with brass standards, the results obtained should, if the set is correct, be the same as if each piece were made of solid brass.* The density of the air varies with the temperature, moisture and carbon dioxide content, barometric pressure, and the value of gravity. Since, however, in chemical work relatively small volumes of materials are used for the weighings, it is not necessary to consider slight variations in these factors.

Ordinarily, the weight of 1 ml of air at room temperature is assumed to be 1.2 mg,† and the density of brass weights is assumed to be 8.0.

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* Although the U. S. Bureau of Standards does certify with respect to the actual masses of some weights that it tests, it also gives the *value of each weight in terms of standard brass weights* when the weighing is made in air under average conditions. A set of weights should, unless otherwise stated, give values in terms of the brass standards. The chemist can assume, therefore, in making correction for the buoyancy of air, that all his weights are made of brass even although some of them may be gold or platinum plated or made of German silver or aluminum.

† For determining the true weights of large masses of materials, as is necessary in some physical experiments, it is necessary to know the density of air with greater

If d_1 denotes the density of the object weighed, d_2 the density of the weights, ρ the weight of 1 ml of air, p_0 the weight in vacuo, and p the weight in air, the weight in vacuo can be found by the following formula

$$p_0 = p + \left(\frac{p_0}{d_1} - \frac{p_0}{d_2}\right)\rho$$

If the density of air is assumed to be 0.0012, which is accurate to only two significant figures, and the density of the substance is given to only two significant figures, not more than three significant figures should be used in the value of p_0 and p in the parenthesis. In this formula, therefore, p_0 can be replaced by p, and we have

$$p_0 = p + \left(\frac{p}{d_1} - \frac{p}{d_2}\right)\rho$$

In using this formula, it is customary to express the density of air, ρ, in milligrams, and if the values of p (in grams) inside the parenthesis are taken to only two significant figures, the correction can be easily found with the aid of the slide rule. In applying this correction to the value p it is necessary, then, to remember that the correction is in milligrams.

Instead of making the computation, the following table of Kohlrausch may be used:

REDUCTION OF A WEIGHING MADE IN AIR WITH BRASS WEIGHTS TO VACUO

d	k	d	k	d	k
0.7	+1.57	2.0	+0.46	8	+0.01
0.8	1.36	2.5	0.34	9	−0.01
0.9	1.19	3.0	0.26	10	−0.02
1.0	1.06	3.5	0.20	11	−0.03
1.1	0.95	4.0	0.16	12	−0.04
1.2	0.86	4.5	0.13	13	−0.05
1.3	0.78	5.0	0.10	14	−0.06
1.4	0.72	5.5	0.08	15	−0.06
1.5	0.66	6.0	0.06	16	−0.07
1.6	0.61	6.5	0.04	17	−0.07
1.7	0.56	7.0	0.03	18	−0.08
1.8	0.52	7.5	0.02	19	−0.08
1.9	0.49	8.0	0.01	20	−0.08
2.0	0.46			21	−0.09

$k = 1.20\left(\frac{1}{d} - \frac{1}{8.0}\right)$ mg. If a substance of specific gravity d weighs g grams in the air, then $g \cdot k$ milligrams are to be added to the weight in

precision. Density tables taken from W. Felgentraeger's *Theorie Konstruktion und Gebrauch der feineren Hebelwage*, and Circular No. 3 of the U. S. Bureau of Standards, will be found on p. 14.

DENSITY OF DRY AIR (MILLIGRAMS PER MILLILITER)

b \ T	16°	17°	18°	19°	20°	21°	22°	23°	24°	25°	26°	27°	28°
690	1.103	099	094	090	086	082	077	073	069	065	061	057	052
1	104	100	096	092	087	083	079	075	071	066	062	058	054
2	106	102	097	093	089	085	081	076	072	068	064	060	055
3	108	103	099	095	091	086	082	078	074	070	065	061	057
4	109	105	101	096	092	088	084	080	075	071	067	063	059
5	111	106	102	098	094	089	085	081	077	073	068	064	060
6	112	108	104	099	095	091	087	083	078	074	070	066	062
7	114	110	105	101	097	093	088	084	080	076	072	067	063
8	116	111	107	103	098	094	090	086	082	077	073	069	065
9	117	113	109	104	100	096	092	087	083	079	075	070	066
700	1.119	115	110	106	102	097	093	089	085	080	076	072	068
1	120	116	112	107	103	099	095	090	086	082	078	074	069
2	122	118	113	109	105	100	096	092	088	084	079	075	071
3	124	119	115	111	106	102	098	094	089	085	081	077	072
4	125	121	117	112	108	104	099	095	091	087	082	078	074
5	127	122	118	114	110	105	101	097	092	088	084	080	076
6	128	124	120	115	111	107	103	098	094	090	085	081	077
7	130	126	121	117	113	108	104	100	096	091	087	083	078
8	132	127	123	118	114	110	106	101	097	093	089	084	080
9	133	129	125	120	116	112	107	103	099	094	090	086	082
710	1.135	130	126	122	117	113	109	105	100	096	092	087	083
1	136	132	128	123	119	115	110	106	102	097	093	089	085
2	138	134	129	125	121	116	112	108	103	099	095	090	086
3	140	135	131	127	122	118	114	109	105	101	096	092	088
4	141	137	132	128	124	119	115	111	106	102	098	094	089
5	143	138	134	130	125	121	117	112	108	104	099	095	091
6	144	140	136	131	127	123	118	114	110	105	101	097	092
7	146	142	137	133	128	124	120	115	111	107	102	098	094
8	148	143	139	134	130	126	121	117	113	108	104	100	095
9	149	144	140	136	132	127	123	119	114	110	106	101	097
720	1.151	146	142	138	133	129	124	120	116	111	107	103	099
1	152	148	144	139	135	130	126	122	117	113	109	104	100
2	154	150	145	141	136	132	128	123	119	114	110	106	102
3	156	151	147	142	138	134	129	125	120	116	112	107	103
4	157	153	148	144	140	135	131	126	122	118	113	109	105
5	159	154	150	145	141	137	132	128	124	119	115	111	106
6	160	156	151	147	143	138	134	130	125	121	116	112	108
7	162	158	153	149	144	140	136	131	127	122	118	114	109
8	164	159	155	150	146	141	137	133	128	124	120	115	111
9	165	161	156	152	147	143	139	134	130	125	121	117	112
730	1.167	162	158	153	149	145	140	136	131	127	123	118	114
1	169	164	160	155	151	146	142	137	133	129	124	120	115
2	170	166	161	157	152	148	143	139	135	130	126	121	117
3	172	167	163	158	154	149	145	140	136	132	127	123	119
4	173	169	164	160	155	151	147	142	138	133	129	124	120
5	175	170	166	161	157	153	148	144	139	135	130	126	122
6	177	172	168	163	159	154	150	145	141	136	132	128	123
7	178	174	169	165	160	156	151	147	142	138	133	129	125
8	180	175	171	166	162	157	153	148	144	139	135	131	126
9	181	177	172	168	163	159	154	150	145	141	136	132	128
740	1.183	178	174	169	165	160	156	151	147	142	138	134	129
1	185	180	176	171	166	162	157	153	148	144	140	135	131
2	186	182	177	173	168	164	159	155	150	146	141	137	132
3	188	183	179	174	170	165	161	156	152	147	143	138	134
4	189	185	180	176	171	167	162	158	153	149	144	140	136
5	191	186	182	177	173	168	164	159	155	150	146	141	137
6	193	188	183	179	174	170	165	161	156	152	147	143	139
7	194	190	185	180	176	171	167	162	158	153	149	144	140
8	196	191	187	182	177	173	168	164	159	155	150	146	142
9	197	193	188	184	179	175	170	166	161	157	152	148	143
750	1.199	194	190	185	181	176	172	167	163	158	154	149	145
1	201	196	191	187	182	178	173	169	164	160	155	151	146
2	202	198	193	188	184	179	175	170	166	161	157	152	148
3	204	199	195	190	185	181	176	172	167	163	158	154	149
4	205	201	196	192	187	182	178	173	169	164	160	155	151
5	207	202	198	193	189	184	179	175	170	166	161	157	152
6	209	204	199	195	190	186	181	177	172	167	163	158	154
7	210	206	201	196	192	187	183	178	174	169	164	160	155
8	212	207	203	198	193	189	184	180	175	171	166	161	157
9	213	209	204	200	195	190	186	181	177	172	168	163	158

DENSITY OF DRY AIR (MILLIGRAMS PER MILLILITER).—*Continued*

b \ T	16°	17°	18°	19°	20°	21°	22°	23°	24°	25°	26°	27°	28°
760	1.215	210	206	201	196	192	187	183	178	174	169	165	160
1	217	212	207	203	198	193	189	184	180	175	171	166	162
2	218	214	209	204	200	195	190	186	181	177	172	168	163
3	220	215	211	206	201	197	192	187	183	178	174	169	165
4	221	217	212	208	203	198	194	189	184	180	175	171	166
5	223	218	214	209	204	200	195	191	186	181	177	172	168
6	225	220	215	211	206	201	197	192	188	183	178	174	169
7	226	222	217	212	208	203	198	194	189	184	180	175	171
8	228	223	219	214	209	204	200	195	191	186	181	177	172
9	230	225	220	215	211	206	201	197	192	188	183	178	174
770	1.231	226	222	217	212	208	203	198	194	189	185	180	175
1	233	228	223	219	214	209	205	200	195	191	186	182	177
2	234	230	225	220	215	211	206	201	197	192	188	183	178
3	236	231	227	222	217	212	208	203	198	193	189	185	180
4	238	233	228	223	219	214	209	205	200	195	191	186	182
5	239	234	230	225	220	216	211	206	202	197	192	188	183
6	241	236	231	227	222	217	212	208	203	198	194	189	185
7	242	238	233	228	223	219	214	209	205	200	195	191	186
8	244	239	234	230	225	220	216	211	206	202	197	192	188
9	246	241	236	231	227	222	217	213	208	203	199	194	189
780	247	242	238	233	228	223	219	214	209	205	200	195	191

air in order to obtain the weight in vacuo. The correction is positive if the substance has a density lower than that of brass and negative if the substance has a higher density than brass. In using the table, remember that the correction is given in milligrams and the weights are usually written in terms of the gram.

The above table* gives the density of air in milligrams per cubic centimeter for air of 50 per cent humidity and for a place where g equals 981.3 cm per sec. The temperature should be that of the balance case, and that of the barometer should not vary by more than 5°.

Calibration of a Set of Weights

A set of weights as furnished by the maker cannot as a rule be relied upon closer than to 0.5 mg for weighings of about 1 g. For exact work in absolute weighing it is necessary to determine not only the relative errors of the weights among themselves but also the absolute error of the set by comparing one of the largest pieces with a standard weight.

Weights are tested by the U. S. Bureau of Standards upon application and the payment of a suitable fee. The Bureau of Standards recognizes six classes of weights. Class T are ordinary trade weights which are not tested by the Bureau except when there is no local authority to whom they can be submitted, or in the event of an important controversy. The laboratory weights used for rough weighings usually belong to this class. Class C weights are more accurate than those of Class T, and the permissible errors are only one-tenth as much. Classes A and B have allowable errors of about one-fifth as much as Class C, but the correction for each weight of

* W. Felgentraeger, *Theorie Konstruktion und Gebrauch der feineren Hebelwage.* Cf. Circular No. 3, U. S. Bureau of Standards.

Class A is determined accurately so that allowance for this error can be made in using the weight.

For the more precise weighings of the chemical laboratory, weights of Class S should be used. Class M weights are recommended for scientific work of the highest possible precision, but when the corrections for each member of a Class S set of weights is known, the set can be used with practically the same accuracy as a Class M set.

The analytical chemist rarely needs to know the absolute weight of anything. Almost all his work is expressed in percentages of an original weight taken. If every weight in the box were exactly twice as heavy as it is marked, the results of analysis would be the same, provided such a set of weights were used exclusively, as if each weight were correct. The chemist, therefore, is much more interested in knowing the relation of the weights to one another than in knowing the actual error of any particular piece. A set of weights calibrated in terms of any weight of the set is satisfactory for the purposes of exact quantitative analysis.

The following method of calibrating a set of weights is that recommended by T. W. Richards.*

The calibration starts with the smallest weight in the set, which is assumed here to be the 10-mg piece. As a temporary standard, it is assumed that one of these 10-mg pieces is correct and the value of every other piece in the set is obtained in terms of it. The weighings are best made by the method of swings, taking three pointer readings at the left of the zero-mark on the scale and two on the right, as described on p. 7. To make sure that the corrections obtained are correct to the nearest 0.1 mg it is advisable to compute each correction to one more decimal place, although this last figure will not be very accurate.

Procedure. — Mark the different weights of the same denomination so that they are recognizable, and always keep them in the same order in the box. Place one of the 10-mg weights on the left scale pan and counterbalance it with any suitable tare, taking care that the rider is not too near either end of the scale. Using the method of swings, determine the rest point of the pointer and the sensitiveness of the balance. Replace the first 10-mg weight with another of like value and determine the amount by which the rider must be moved to attain the same rest point, recording the difference to 0.01 mg. If the weights are practically the same, as they should be, this is best done not by actually moving the rider but from the displacement of the rest point as described under weighing by the *Method of Swings* (p. 8).

If the second weight is found heavier than the first it is given a positive correction in this comparison. To make sure that the balance has remained in a constant condition during this trial, test the original weight again.

Next place the two 10-mg pieces on the left pan and counterbalance them with a suitable tare. Replace the two small pieces with a 20-mg weight and find its value in terms of the two smaller ones. Proceed in the same way with every weight in the box.

* *J. Am. Chem. Soc.*, **22**, 144 (1900).

Assume for the purpose of calculation that the first 10-mg weight is correct* and establish the value of all the other weights on this assumption. The values thus computed are consistent among themselves but are usually quite different from the face values of the individual weights. This is because the original standard is too small. It is better to assume that one of the larger weights is correct and, in fact, this may be compared with a weight that has been standardized by the Bureau of Standards at Washington, although this is wholly unnecessary for most purposes. From the assumed, or corrected, value of one of the larger weights, compute what the corresponding calibration correction should have been for each of the smaller weights. Thus if the calibration correction for the 10-g weight was found to be +0.01768 g and it is now assumed to be correct, the 1-g weight stands in its proper relation to the 10-g weight if its calibration correction was found to be +0.00177 g. If its calibration correction was found to be less, then the weight is too light and a negative correction should be applied in using it.

The following table shows all the data and the results obtained in a typical calibration. In the first column the weights are named by their face values. In the second column the calibration values are given as obtained with one of the smallest weights as standard of comparison. These values are copied from a notebook in which each de-

CALIBRATION OF WEIGHTS

Face Value in Grams	Calibration Value	Ideal Calibration Value	Correction in Milligrams
0.01	Temporary Standard	0.01002	−0.02
0.01′	0.01006	0.01002	+0.04
0.01″	0.01005	0.01002	+0.03
0.02	0.02005	0.02004	+0.01
0.05	0.05009	0.05009	0.00
0.1	0.10019	0.10018	+0.01
0.1′	0.10020	0.10018	+0.02
0.2	0.20035	0.20035	0.00
0.5	0.50088	0.50088	0.00
1	1.00183	1.00177	+0.06
2	2.00383	2.00354	+0.29
2′	2.00368	2.00354	+0.14
5	5.00884	5.00884	0.00
10	10.01768	10.01768	Final Standard
10′	10.01740	10.01768	−0.28
20	20.03520	20.03536	−0.16
50	50.08790	50.08840	−0.50

* Hopkins, Zinn and Rogers, *J. Am. Chem. Soc.*, **45**, 2528 (1920), recommend checking the observations against standard 50-, 5-, 1-, 0.1-, and 0.001-mg weights. This makes it simpler for a beginner and easier to divide the work into several periods and also to some extent does away with compensating errors. Double weighing is also a little easier than weighing against a tare. Cf. P. Weatherell, *ibid.* **52**, 1938

tail of each weighing was recorded. The third column gives the ideal value of each weight when the 10-g piece is taken as the permanent standard, and the fourth column gives the correction that must be applied to each weight.

Prepare a card from the individual corrections to show the corrections which should be applied to the usual combinations from 0.01 to 1.00 g and from 1 g upward, and keep this card in the balance case. In an ordinary gravimetric analysis, record the weights as follows:

	Observed Weight	Corrected Milligram	Corrected Weight
Weight crucible + substance.......	19.3105	$\begin{Bmatrix} +0.39 \\ -0.01 \end{Bmatrix}$	19.3109
Weight crucible alone..............	16.9916	$\begin{Bmatrix} + .06 \\ + .06 \end{Bmatrix}$	16.9917
Weight of substance...............			2.3192

The upper correction is that of the weights of 1 g and over; the lower is that of the fractional weights.

METHOD OF KOHLRAUSCH

The method of Kohlrausch depends upon the assumption that the sum of the 50, 20, 10, 10′, 5, 2, 1, 1′ and 1″ pieces is exactly 100 g. It is best to weigh by the *method of swings*, and correction for unequal balance arms should be made by *double weighing*, weighing by substitution, or by use of the *balance arm ratio*. When two or more weights of the same denomination are present in the set, they should be marked so that they may be distinguished from one another.

Procedure. — Starting with the largest weight find its value in terms of the smaller ones, and continue in the same way with all the other weights of 1 g and over

$$\begin{aligned} 50\text{ g} &= 20 + 10 + 10' + 5 + 2 + 1 + 1' + 1'' + A\text{ mg} \\ 20\text{ g} &= 10 + 10' + B\text{ mg} \\ 10' &= 10 + C\text{ mg} \\ 5 + 2 + 1 + 1' + 1'' &= 10 + D\text{ mg} \end{aligned}$$

With the aid of these equations, express the weights in terms of the 10-g piece.

$$\begin{aligned} 5 + 2 + 1 + 1' + 1'' &= 10\text{ g} \quad + D\text{ mg} \\ 10 &= 10 \\ 10' &= 10 \quad + \quad C \\ 20 &= 10 + 10 + \quad C + B \\ 50 &= 10 + 10 + 10 + 10 + 10 + A + B + 2C + D \end{aligned}$$

If it is assumed that the sum of the left-hand members of these last expressions is equal to exactly 100 g, then the sum of the right-hand members must also equal 100 g. We have $10 \times \mathbf{10} + A + 2B + 4C + 2D = 100$ g, and the 10-g weight itself:

$$\mathbf{10} = 10 - \frac{A + 2B + 4C + 2D}{10}$$

If we let $S = \dfrac{A + 2B + 4C + 2D}{10}$, then we obtain

$$\begin{aligned}
\mathbf{10} &= 10\text{ g} - S \\
10' &= 10\text{ g} - S + C \\
5 + 2 + 1 + 1' + 1'' &= 10\text{ g} - S + D \\
20 &= 20\text{ g} - 2S + B + C \\
50 &= 50\text{ g} - 5S + A + B + 2C + D \\
&= 50\text{ g} + \tfrac{1}{2}A
\end{aligned}$$

The sum $\frac{1}{2}A + B + 2C + D - 5S$ should equal 0, which serves as a test for the accuracy of the observations.

Now compare the 5-g weight with the $2 + 1 + 1' + 1''$ in exactly the same way:

$$\begin{aligned}
5 &= 2 + 1 + 1' + 1'' + a \\
2 &= 1 + 1' + b \\
1' &= 1 + c \\
1'' &= 1 + d
\end{aligned}$$

According to the preceding work

$$5 + 2 + 1 + 1' + 1'' = 10.000 - S + D$$

consequently

$$10 \times 1 + a + 2b + 4c + 2d = 10.000 - S + D$$

and

$$1 = 1.000 - \frac{a + 2b + 4c + 2d + S - D}{10}$$

If we let $s = \dfrac{a + 2b + 4c + 2d + S - D}{10}$, we obtain

$$\begin{aligned}
1 &= 1.000 - s \\
1' &= 1.000 - s + c \\
1'' &= 1.000 - s + d \\
2 &= 2.000 - 2s + b + c \\
5 &= 5.000 - 5s + a + b + 2c + d
\end{aligned}$$

In the same way test the smaller weights until finally the following correction table is obtained.

TABLE FOR CORRECTION OF WEIGHTS

$50 = 50\,g + \frac{1}{2}A$ $20 = 20\,g - 2S + B + C$ $10 = 10\,g - S$ $10' = 10\,g - S + C$	$\underbrace{5 + 2 + 1 + 1' + 1''}_{10} = 10\,g - S + D$	$\underbrace{0.5 + 0.2 + 0.1 + 0.1' + \Delta^*}_{1} = 1\,g - S + \alpha$	$\underbrace{0.1}_{} \; \Delta = 0.1\,g - s' + \sigma$
$\left.\begin{matrix}5\\2\\1\\1'\\1''\end{matrix}\right\} = 10\,g - S + D$	$5 = 5\,g - 5s + a + b + 2c + d$ $2 = 2\,g - 2s + b + c$ $1 = 1\,g - s$ $1' = 1\,g - s + c$ $1'' = 1\,g - s + d$	$0.5 = 1\,g - 5s' + \beta + \gamma + 2\delta + \sigma$ $0.2 = 0.2\,g - 2s' + \gamma + \delta$ $0.1 = 0.1\,g - s'$ $0.1' = 0.1\,g - s' + \delta$ $\Delta = 0.1\,g - s' + \sigma$	$0.05 = 0.5\,g - 5s'' + l + m + 2n + o$ $0.02 = 0.02\,g - 2s'' + m + n$ $0.01 = 0.01\,g - s''$ $0.01' = 0.01\,g - s'' + n$ Rider $= 0.01\,g - s'' + o$
Sum = 100 g	$10\,g - S + D$	$1\,g - s + \alpha$	$0.1\,g - s' + \sigma$

* $\Delta = 0.05 + 0.02 + 0.01 + 0.01' +$ rider on the 10-mg division.

When weights are tested at the U. S. Bureau of Standards, the desired accuracy is shown by the following table.

Denomination	Precision of Corrections	Tolerance	Denomination	Precision of Corrections	Tolerance
kg	g	mg	mg	mg	mg
20	0.1	100	500	0.01	0.05
10	0.01	50	200	0.01	0.05
5	0.01	30	100	0.01	0.05
2	0.01	10	50	0.01	0.03
	mg		20	0.01	0.03
1	5 or 1	5	10	0.01	0.02
g			5	0.01	0.02
500	1	3	2	0.01	0.01
200	1	1	1	0.01	0.01
100	0.5 or 0.1	0.5	0.5	0.01	0.01
50	0.1	0.3	0.2	0.01	0.01
20	0.1	0.2	0.1	0.01	0.01
10	0.05	0.15			
5	0.05	0.15			
2	0.05	0.10			
1	0.05 or 0.01	0.10			

Weighing Samples of Factor Weights. — In a busy laboratory it is often desirable to weigh out samples in such a way that the results of the analyses are known with as little computation as possible. Thus if the iron content of a sample weighing 0.6994 g is determined by weighing ferric oxide, Fe_2O_3, the percentage of iron, Fe, is exactly 100 times the weight of the oxide. If 1 ml of standard hydrochloric acid will neutralize 0.028 g of pure sodium carbonate, then the percentage purity of a sample of sodium carbonate, containing no other substance of basic nature, will be just twice the number of cubic centimeters of acid used in the analysis of samples weighing 1.4 g. In every technical laboratory, therefore, the chemist has to learn to weigh out rapidly

samples of specified weights. If the sample is a dry powder, unaffected by contact with the air, it can be weighed out on a watch glass. It is convenient to have a pair of counterpoised watch glasses for this purpose, *i.e.*, a pair of watch glasses which weigh so nearly alike that they can be balanced with the aid of the rider.

Place on the left balance pan the watch glass which is to hold the substance and on the right pan place the tare of the watch glass and additional weights amounting to the desired quantity. With the aid of a small spatula, or a palette-knife, transfer some of the powder to the watch glass in the left pan, until the pointer swings to the right with the beam lowered slightly so that the pointer can swing but a little way. Raise the beam, remove a little of the powder, and, with the beam again lowered a little, add more powder by tapping the spatula. By repeating this process once or twice and finally testing with the balance beam altogether lowered, it is possible to get any desired weight within one or two tenths of a milligram. In chemical work it is a waste of time to try to make the original weight much more accurate than the rest of the analysis. Thus in determining the carbon content of a sample of steel with approximately 1 per cent of carbon present, the results of duplicate analyses with equal weight samples would be considered satisfactory if they indicated 1.00 and 1.01 per cent of carbon. In other words, errors arising from lack of homogeneity and inaccuracies in the method of analysis may easily amount to 1/100 of the total carbon content. An error of 0.01 g in the weight of a gram sample of the steel would be no greater than the allowable error of the analysis. In weighing out the sample, therefore, if the weight is accurate to the nearest centigram the error is less than that of the remainder of the work. On the other hand, in determining the chlorine content of a sample of salt weighing about 0.25 g it is important to get the weight to the nearest tenth of a milligram because the chlorine determination can be accomplished with an accuracy of one part in one thousand with samples of this size.

Reliability of a Result.* — In order that the result of any measurement may be of scientific or technical value, it is desirable to have some numerical estimate or measure of its validity. By the *accuracy* of a result should be understood the degree of concordance between it and the true value of the quantity measured. The true value is not usually known so that it is not always possible to obtain a numerical measure of the absolute accuracy of a measurement or analysis. By the *precision* or *precision measure* of a result is understood the best numer-

* The following discussion is based upon H. M. Goodwin's *Elements of the Precision of Measurements.*

ical measure of its reliability after all known sources of error have been eliminated or allowed for.

When any quantity is measured to the full precision of which the instrument or method is capable, it will usually be found that the results of repeated measurements do not agree exactly. Thus in the analysis of pure salt, the chlorine content will not always be found to be exactly 60.66 per cent although we may have reason to believe that this is the correct value.

All that we can hope to obtain from experimental data is the most probable value of the quantity or quantities in question. The branch of mathematics which treats of the general problem of the adjustment of errors of observation so that their effect upon the final result is reduced to a minimum is called *least squares*. According to the theory, the most probable values of a series of related observations are those for which the sum of the squares of the errors is a minimum. Here is not the place to go into the details of the mathematical proofs of the method of least squares, but it is important that every chemist should keep constantly in mind certain deductions that have been made from such studies.

In a series of observations, all of which possess an equal degree of probability, the most probable value of the quantity is the arithmetical mean. Since the true value of the quantity is not known in most cases, the error of each determination and of the mean cannot be determined. It is possible, however, to state how far each observation differs from the mean value, and from these differences the *probable deviation* of the mean can be estimated. The average deviation of the mean, usually designated as *ad*, is determined by dividing the sum of the deviations from the mean by the number of determinations made. The *ad* may be regarded as a numerical measure of the amount by which a new observation is likely to differ from the mean value, m.

Since the mean has a higher degree of probability than any single observation, it should have a smaller deviation from the truth. It can be shown that an arithmetical mean computed from n equally reliable observations is $\sqrt{n}$ times as reliable as any one observation. The deviation of the mean is usually denoted as AD. According to the statement just made,

$$AD = \frac{ad}{\sqrt{n}}$$

A little study of this expression shows that it does not pay to increase the number of observations beyond a certain limit as the time and labor involved soon become excessive.

It is probable that more than half the time spent on chemical and physical computations is wasted owing to the retention of more figures than the precision of the data warrants. The habit should be acquired of rejecting at each stage of the work all figures which have no influence on the final result. In the following rules for computation the term *digit* denotes any one of the ten numerals including the zero, and the term *significant figure* is any digit which denotes or signifies the amount of the quantity in the place in which it stands. Thus a zero may or may not be a significant figure. When it is used merely to locate the decimal point as in the values 1000 and 0.001, the zero is not a significant figure, for the position of the decimal point is determined solely by the unit in which the quantity is expressed. There are two significant figures in the value 2.5 mg even when it is written 0.0025 g. The number of decimal places in a result has in itself no significance in indicating the precision of a measurement. The statement that the results of an analysis agree within 1.2 mg gives no idea of the precision unless the entire value is known. A fractional or percentage precision measure, on the other hand, gives a definite idea of the precision of the measurement as it involves both the value of the quantity and its average deviation.

Rules for Computations

Rule I. In rejecting superfluous figures, increase by 1 the last figure retained if the following figure (that has been rejected) was 5 or over.

Rule II. In all deviation and precision measures retain two, and only two, significant figures.

Rule III. Retain as many figures in a mean result, and in data, as correspond to the second place of significant figures in the deviation or precision measure. According to this rule, two places of unreliable figures are retained in data so that accumulated errors due to rejections in the course of computation will not affect the first place of uncertain figures. Or, looked at from another point of view, the last figure may be regarded as quite unreliable but the next to the last significant figure should not vary by more than *one* or at the most *two* units from the mean.

Rule IV. The sum or difference of two or more quantities cannot be more precise than the quantity having the largest deviation. In adding or subtracting quantities, find the *ad* of each and retain in each quantity as many places as correspond to the second place of significant figures in the quantity with the largest deviation.

Rule V. In multiplication or division, the percentage precision of the product or quotient cannot be greater than the percentage precision of the least precise factor entering into the computation. Hence, determine the percentage precision of the least reliable factor. If this is about 10 per cent or better, use three significant figures in each factor of the computation and in the final result. If 1 per cent or better, use four significant figures in each factor of the computation and in the final result. If 0.1 per cent or better, retain five significant figures.

For computations involving a precision not greater than about 0.25 per cent use a 10-inch slide rule.

Rule VI. In carrying out the operations of multiplication and division by logarithms, retain as many places in the mantissa of the logarithm of each factor as are properly retained in the factors themselves under Rule V.

In ordinary chemical work the percentage precision of the result is often less than 0.1 per cent. Thus, in the determination of the chlorine content of a sample of pure salt weighing about 0.2 g, check values of 60.60 and 60.72 per cent chlorine would usually be considered satisfactory. This corresponds to a *percentage precision* of 0.12 part in 61.0 or 0.2 per cent. According to the above rules, only *four* figures should be retained in all factors entering into this computation, and four-place logarithms should be used. In the computation, the molecular weight of silver chloride should be taken as 143.3 instead of 143.34. If, on the other hand, a series of determinations all gave values ranging between 60.63 and 60.69 per cent chlorine, one would be justified in keeping *five* significant figures and using five-place logarithms. This would not necessarily mean that the original weight of the salt and the final weight of the precipitate would have to be carried out to five significant figures because an error of 0.0002 g in about 0.2 g of salt would only correspond to 0.1 per cent of the entire weight. One would be justified, however, in recording the weights to five decimal places, using the method of swings.

For most chemical work, four significant figures are sufficient. In some cases, as in the determination of sulfur in steel, or in the conversion of small volumes of a solution (less than 1 ml) into an equivalent volume of some other solution, only two significant figures should be used.

Filtration and Washing of Precipitates

How large should the filter be, and how many times should the precipitate be washed?

With regard to the second question it is evident that the precipitate should be washed until the soluble, non-volatile matter is completely

removed. It is clear, however, that this point will never be reached because a part of the solution always remains on the filter, but it is not difficult to make the amount of the dissolved substance remaining so small as to be negligible. When the amount of dissolved substance remaining on the filter is so small that it could not be detected by the balance, the precipitate can be considered to be completely washed.

The aim should be not only to remove the soluble matter, but also to accomplish this with as little wash water as possible.

No precipitate is absolutely insoluble, so that it is clear that every unnecessary excess of wash water causes harm by removing a fraction of the precipitate, and the greater the excess of the wash water the greater the amount of the precipitate dissolved.

The amount of wash water to be used depends largely upon the nature of the precipitate itself. Amorphous, gelatinous precipitates always require more washing than crystalline, granular ones.* As a rule, it may be said that the process of washing must be continued until the substance which is being washed out can no longer be detected in the last filtrate. If the filtrate must be used for another determination, it is obvious that it should not be tested too soon.

Let us assume the filter to hold 10 ml, the solution to drain to the last drop from the paper, the amount of the solution held back by the precipitate and filter to be 1 ml and to contain 0.1 g of the solid substance which is to be removed by washing.

The filter is filled to the upper edge with wash water and allowed to drain to the last drop n times, until not more than 1/100 mg of the substance to be removed by washing remains.

According to our assumption, 9 ml drain off and 1 ml remains behind; we have consequently:

Removed by the			There remains after the		
1st	washing,	$0.1 \cdot 9/10$ g	1st	washing,	$0.1 \cdot 1/10$ g
2d	"	$0.1 \cdot 9/10 \cdot 1/10$ g	2d	"	$0.1 \cdot 1/10 \cdot 1/10$ g
3d	"	$0.1 \cdot 9/10 \cdot (1/10)^2$ g	3d	"	$0.1 \cdot 1/10 \cdot (1/10)^2$ g
nth	"	$0.1 \cdot 9/10 \cdot (1/10)^{n-1}$ g	nth	"	$0.1 \cdot 1/10 \cdot (1/10)^{n-1}$ g

After washing n times, therefore, the amount removed by washing is the sum of the decreasing geometric series of which the first term is $0.1 \cdot 9/10$ and the constant factor is 1/10.

* The reason why some precipitates require more washing than others is that the degree of adsorption varies as will be explained.

If $n = 4$, the sum of the series is

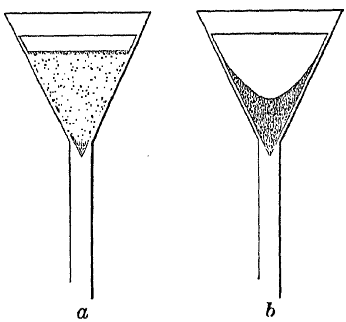
$$\Sigma = \frac{0.1 \cdot \frac{9}{10}[(\frac{1}{10})^4 - 1]}{\frac{1}{10} - 1} = 0.09999 \text{ g}$$

After the precipitate has been washed four times, therefore, 0.09999 g of the impurity has been removed. According to the assumption that there was originally 0.1 g of this substance, there remains in the precipitate only 0.00001 g, or in other words a negligible amount.

Consequently, the filtrate should be tested qualitatively for the substance to be removed only after the precipitate has been washed four times.

Often the washing will be found to have been complete after the fourth washing, but as a rule this will not be so, and frequently it will be found necessary to repeat the operation ten to twenty times. In the processes which are described it will usually be stated how far to carry the washing.

Now in order to wash a precipitate with the least possible amount of wash water, it is evident that the size of the filter paper will have an effect. The filter should be made as small as possible, irrespective of whether there is little or much liquid to filter. *The size of the filter used should be regulated entirely by the amount of the precipitate and not at all by the amount of the liquid to be filtered.* The mistake should not be made, however, of using too small a filter. The precipitate should never reach the upper edge of the paper; about 5 mm should remain free, and even then the filter should not be so completely filled as in Fig. 5*a*. It is better to have the filter filled about as much as is shown in Fig. 5*b*, in order that sufficient room is left for the wash water.



a *b*

FIG. 5.

The use of too large filters is one of the inexcusable analytical errors.

Adsorption by Precipitates. — Whenever substances are in intimate contact with one another there is always a tendency for a slight change in concentration (quantity present in a unit volume) at the place of contact. This phenomena is called *adsorption*, and the term differs from the closely related word *absorption* by meaning especially the change that takes place at the exposed *surfaces*. The 1901 edition of the Century Dictionary defined adsorption as " condensation of gases

on the surfaces of solids," but the term is no longer restricted in this way, and there may be adsorption of vapor by a liquid, of liquid by solid, and of solid by liquid. Of special interest to the analytical chemist is the adsorption from solution by a solid. In cases of adsorption there is usually more or less fixation at the surface but sometimes there is a tendency for the adsorbed material to penetrate into the adsorbent.

Since adsorption is primarily a surface phenomenon, it is not strange to find that the extent of the adsorption is determined largely by the amount of exposed surface. Subdivision always increases the surface of a solid. Thus Wolfgang Ostwald* has computed that a cube with edges 1 cm long and exposing only 6 sq cm of surface will have 6 sq m of surface if broken into 10^{12} smaller cubes each with an edge of 1 μ (0.001 mm). According to the same author a colloidal solution which will pass through a paper filter contains particles of suspended material ranging from 0.1 μ to 1 mμ (0.001 μ).

When the adsorbing surface is relatively small, as with the sides of a glass vessel or with a small filter paper, errors caused by adsorption are usually not serious and it is comparatively easy to wash free from the adsorbed material. In crystalline precipitates with large grains the errors are not usually as serious as in *gels* such as ferric or aluminum hydroxide. Adsorption is always more or less selective in nature, and precipitates tend to adsorb some substances in solution to a much greater extent than they do others. In fact, sometimes there is what is called *negative adsorption*, although this is of less importance than the more common *positive adsorption* which may cause serious errors in chemical analysis. It has been shown that aluminum hydroxide will decolorize dilute solutions of alizarine and certain other dyestuffs but has practically no adsorbing action on emerald green or chrysoidine. Freshly precipitated, hydrated aluminum hydroxide and metastannic acid are capable of adsorbing large quantities of arsenic acid from solution, and it is practically impossible to remove an appreciable quantity of the adsorbed material by washing. In all cases that have been studied quantitatively, the adsorption is expressed fairly well by the equation

$$\left(\frac{x}{m}\right)^n = kc$$

in which x is the amount adsorbed, m represents the units of adsorbing agent, c is the concentration of the solution, k is a constant, and n is greater than 1 but is not necessarily an integer. As a general rule, the adsorption by a precipitate is less if the solution is dilute and if the precipitate is not allowed to remain long in contact with the solution.

* *Theoretical and Applied Colloid Chemistry.*

In handling colloidal substances adsorption is not the only thing that the chemist has to fear. Most colloids are to some extent reversible and tend to return to the *sol* state when washed with pure water. The sol condition represents a finer state of subdivision than that of the *gel*. To prevent colloidal substances from passing through the filter, it may be desirable to wait for some time before filtering, or to work with fairly concentrated solutions, to wash with the solution of an electrolyte instead of with pure water and to keep the mother liquid hot.

Since one of the most characteristic properties of colloids is the size of the individual particles, it is possible to obtain under some conditions almost any substance in the colloidal state. Many changes that have been attributed to chemical action in the past are known to be due merely to adsorption effects and to changes in the state of subdivision of the substance. It is impossible always to predict how a colloid will behave under conditions which have not been tested with the particular substance in question. Apparently, very few general rules can be applied.

Paper Filters. — Strength, uniform texture, proper porosity, and a low ash are the desirable qualities in filter paper for quantitative work. A paper of 7-cm diameter should have an ash of less than 0.05 mg. To get this low ash, the paper is washed with hydrochloric and hydrofluoric acids. This washing makes the paper softer and more porous but weakens it so that it is more easily torn.

The purpose of filtration is to separate a solid from the liquid in which it is suspended. The pores of the paper must be smaller than the particles of solid which are to be retained by the filter. Precipitates vary with respect to the size of the smallest particles. Some, like crystalline barium sulfate or gelatinous metastannic acid, are very finely divided and require a fine-grained paper. Such filter paper is a slow filtering medium. Consequently chemists are accustomed to use different grades of filter paper, some which make rapid filters and others which make slow filters but are required for precipitates that are likely to pass through the pores of a rapid filter paper.

Funnels are supposed to have an angle of exactly 60°, and the simplest way to fold a circular cut paper is to crease it across a diameter and then, without opening the paper, make a second fold at right angles to the first one. To test the funnel, and this should always be done before starting to filter, open the filter so that it makes a cone to fit the funnel, wet the paper, and see if it fits tightly against the side walls of the funnel. It is important that it should fit tightly along the upper edge which must always be below the rim of the funnel as otherwise the filter cannot be washed satisfactorily. Pour water into the funnel, and if the

filter fits, the stem should fill with liquid. If the stem is too wide, this will not always happen. A little grease in the stem of the funnel will also interfere. If the filter does not fit when folded into a 60° cone, change the second fold sufficiently to make it fit.

It is convenient to mark the funnel so that it can always be told how much the second fold should be changed to make the filter paper fit the funnel. It is also well to mark the funnel so that it can be recognized as a rapid or as a slow funnel, for funnels vary greatly in this respect.

The above method of folding a filter paper is the easiest and quickest but often considerable time is saved in the filtration by folding the paper so that liquid passes through it more rapidly. The following method of folding a filter accomplishes this end but it is harder to make the filter fit tightly to the funnel and there is more danger of having a little precipitate get by the filter.

(1) Fold the paper evenly across a diameter of the circle as in the above method.

(2) Open up the fold and make another at right angles to it creasing the paper on the same side as at first. This is done by merely bringing the two points on the circumference of the circle that were met by the first fold over against one another and flattening out the paper again.

(3) Turn the paper over and fold again exactly $22\frac{1}{2}°$ away from one of the first two folds. To get this position, bisect one of the quadrants formed by the previous two folds, by merely bringing two creases together and flattening out the paper so that a little crease is made on the circumference, and make another bisection in the same way. At this last mark fold across the paper with the crease on the opposite side to that made by the original folds.

(4) Open up the paper and make another fold at right angles to the third fold. Change half of this last fold to make the paper fit the funnel.

For large funnels a *plaited or fluted filter* is often desirable. These can be purchased already folded but the quality of the paper is not always suitable for quantitative work. Swedish filter paper is satisfactory for most purposes when the filter itself is not to be ignited. This can be purchased in sheets and one quarter sheet is sufficient for a large funnel. Since all filter paper retains some of the solution poured through it so firmly that it is very difficult to remove the last traces of solute by washing, it is never wise to choose a large funnel simply because considerable liquid has to be filtered. To make a plaited filter:

(1) Fold the filter once along a diameter as in the first method. Do not open this fold.

(2) Make a second fold along the radius as in the first method.

(3) Open this second fold an[illegible] angles

to each other, dividing the doubled filter into quarters. This is accomplished by taking half of the straight edge of the once folded filter and folding it over to make it coincide with the second fold. In all these folds, take care to make them accurately but do not crease the paper hard at the center.

(4) With the paper again folded only once, make a fold dividing one of the outside segments into halves and make a fold at right angles to this by bringing over the other half of the straight edge.

(5) Make two more folds starting with the other outside segment.

By these seven folds the original circle is divided into 16 parts of equal size and if the paper is opened, half of the creases will be found all on the same side in one half of the paper and all on the other side in the other half of the paper.

(6) With the paper again doubled as it was after the first fold, start at the outside, fold over into the first crease and then bring back the outer edge so that it is in line with the outer edge of the first crease. This makes a subdivision of the outside segment and brings the crease on the opposite side of the doubled paper.

Without opening this last fold, go into the next crease and again come back continuing until the middle fold is reached.

Start in the same way at the other side of the doubled paper and plait toward the center as from the other side.

In this way the paper will be divided into 32 equal segments. If the filter is made from a quarter sheet of Swedish paper, it is not necessary to cut out a circle at the start. When the plaiting is finished it is easy to tear off the ends of the folded paper so that it will fit into the funnel, without protruding above the edge, and leave a nearly circular edge.

Plaited filters are used chiefly when it is desired to filter off a large and bulky precipitate and it is not necessary to wash the precipitate thoroughly. Plaited filters made from Swedish paper filter rapidly but are likely to break at the point of the cone.

It is rarely advisable to use suction with a paper filter. The suction is likely to draw small particles of the precipitate into the pores of the paper and then filtration is usually as slow as or slower than it would have been without the suction. If suction is used with a paper filter, it should rest in a filtering cone made of platinum, palau, or a hardened parchment filter.

Wash-Bottles

For transferring a precipitate to a filter and for washing it, a *wash-bottle* is indispensable. Figure 6 shows a sketch of the type most

commonly used. It consists of a flat-bottomed, 750-ml flask fitted with a rubber stopper and glass tubing bent so that the mouthpiece and outlet tubing are in line. It is best to make the outlet tube in two pieces so that the jet can be manipulated by moving two fingers of the same hand that holds the bottle. The nozzle may be made by drawing out tubing until a capillary is formed and then cutting off to make a stream of the proper size. A stouter tip may be made by simply fusing the end of the original tubing until it has contracted to the proper diameter.

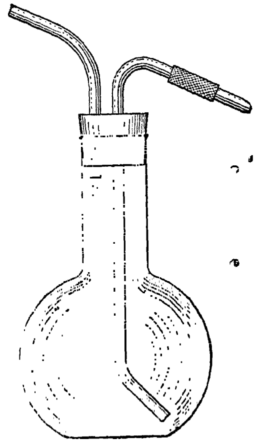


FIG. 6.

The bend of the long piece of tubing inside the flask is made so that this reaches into the deepest part of liquid when the wash-bottle is inclined slightly as in washing precipitates. A bend of the opposite kind is useful for washing precipitates out from beakers, when the bottle is inclined in the opposite direction.

In washing the filter, the stream should always be directed against the upper edge of the paper; this is the hardest part of the paper to wash.

For washing with organic solvents that dissolve rubber, a bottle with a ground-glass stopper is desirable but it is unnecessary for most work in inorganic chemistry.

Policemen

Sometimes a little precipitate adheres to the side of a vessel. To remove it, a piece of rubber over the end of a glass stirring-rod is used. This so-called *policeman* may be made by sticking together the end of a piece of rubber tubing that fits the rod tightly, or it may be purchased from a chemical supply house. The policeman should not as a rule be used for stirring a solution and should not be allowed to remain in solutions.

The Drying and Igniting of Precipitates

Before a precipitate can be weighed it must be absolutely dry. Those precipitates which do not undergo a change of weight on ignition are treated as follows:

(a) THE PRECIPITATE IS IGNITED DRY

This method, in which the precipitate is separated from the filter, the filter burnt by itself, the ash added to the main part of the precipitate, and the mixture then ignited to constant weight, is used when the

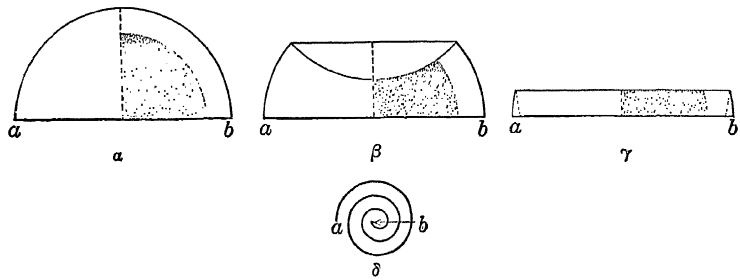


FIG. 7.

ignited substance will be reduced by the burning paper, for example, in the case of precipitates of silver chloride, lead sulfate, bismuth oxide, etc.

To perform this operation it is first desirable to dry the filter and precipitate at 100°. Wet a common filter, stretch it over the top of the funnel, and then gently tear off the superfluous paper. The cover thus formed continues to adhere after drying. Place the funnel and filter in a drying-closet and dry at 100–105°. When perfectly dry, place a weighed crucible upon a piece of glazed paper of about 20 sq cm (Fig. 8, left) and carefully shake the dry precipitate into the crucible, removing it from the paper as completely as possible by gentle rubbing with a platinum spatula. Brush into the crucible with the aid of a feather any small particles of the precipitate which may have fallen upon the glazed paper (Fig. 8). Small particles of the precipitate will still always adhere to the paper, and these must be weighed. In order to accomplish this, set fire to the filter and weigh the ash by itself or mixed with the main part of the precipitate.*

The combustion of the filter, to which small particles of the precipitate still adhere, is best accomplished by the method proposed by Bunsen as follows: Fold the filter together so that the precipitate occupies the position indicated in the shaded part of Fig. 7 α, and then fold again as indicated by β and γ of Fig. 7 to a narrow strip. Roll up the paper

* By using filter paper which has been carefully washed with hydrochloric and hydrofluoric acids, it is permissible to neglect the weight of the ash from the filter itself. With an unknown paper it is necessary to determine the weight of the ash by a separate experiment and then correct the weight of the precipitate obtained.

as indicated by δ, beginning at *b*, so that the portion of the filter which is free from the precipitate is on the outside. Place the roll in the loop of a platinum wire, hold it over the crucible (see Fig. 8), and set fire to the filter by means of the gas-flame. Take away the flame and allow

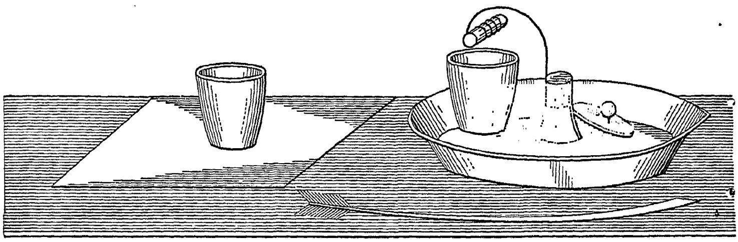


FIG. 8.

the paper to burn quietly. If carbonized particles still remain, apply the gas-flame repeatedly until it is no longer possible to make the particles glow any more. (Too strong ignition should be avoided.) Add the ash to the contents of the crucible by gentle shaking and the final use of the feather. Heat the crucible at first with a small flame, and gradually raise the temperature until the prescribed temperature of ignition for the given precipitate is reached. Finally remove the flame, allow the crucible to cool somewhat, and while still *warm*, but *not glowing*, place it in a desiccator (Fig. 9).

After cooling (at least three quarters of an hour for porcelain crucibles and 20 minutes for platinum ones) weigh the crucible and its contents.

Many precipitates (silver chloride, lead sulfate, etc.) are partially reduced to metal by the above treatment. As these metals are difficultly volatile, however, there will be no loss of the metal, only of the anion (chlorine in the case of silver chloride and SO_4 in the case of lead sulfate). This loss may be readily replaced. Moisten the metal in the crucible with a few drops of nitric acid to dissolve it, add a few drops of hydrochloric acid (in the case of a silver chloride precipitate), or of sulfuric acid (in the case of lead sulfate), and after evaporating off the excess of the acid, weigh the crucible. The only danger in this method is that in burning the filter the ash is heated too hot, so that some of the reduced metal melts and alloys with the platinum wire. If, however, the filter paper is rolled up as

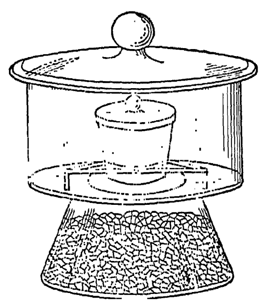


FIG. 9.

was directed, there is always some paper free from precipitate between the precipitate and the platinum wire, yielding an ash which, although its weight is inappreciable, is still sufficient to protect the wire and prevent the reduced metal from coming in contact with it, provided it is not heated strongly enough to melt the metal.

Many precipitates (K_2PtCl_6, etc.) are changed so much by this treatment that it would be impossible to obtain correct results. In such

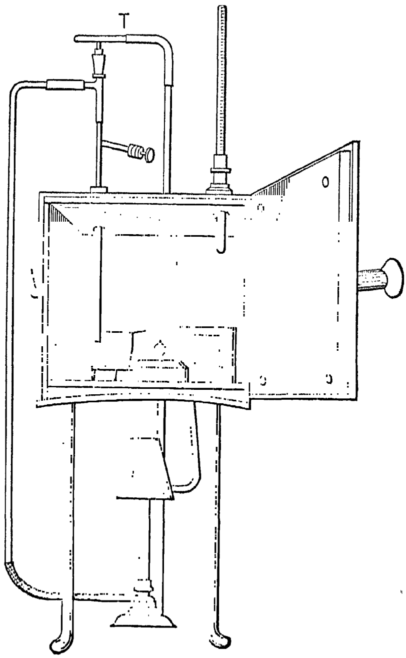


FIG. 10*a*.

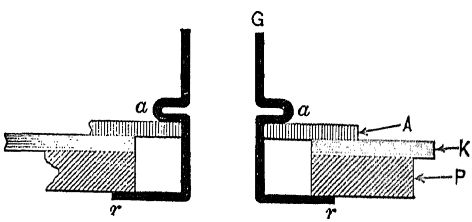


FIG. 10*b*.

cases the filter cannot be burnt, but it is previously dried at a definite temperature and weighed; afterwards the precipitate and filter are again dried at the same temperature and weighed again.

For drying precipitates an electric oven with automatic temperature control is most advantageous. The regulator can be set at the desired temperature which will be maintained indefinitely within a few degrees.

A gas-heated drying oven is shown in Fig. 10. It is fitted with six removable porcelain plates which prevent any oxide falling from the metallic closet walls upon the substance to be dried, rendering it impure. The upper plate has two holes bored in it through which thermometer and thermo-regulator are placed. This upper plate is fastened to the top of the oven as follows: A glass rod, provided with a broad rim *rr* and an enlargement at *aa*, is pushed up through the opening *P* of the porcelain plate and *K* of the upper wall, and this is fastened by placing an asbestos ring *A* between *aa* and *K*.

The bottom plate rests upon a heavy iron wire so that it does not come directly in contact with the bottom of the closet. As the plates can be easily taken out, it is possible to clean them without difficulty. The only part of the apparatus that wears out is the bottom; that it is best to have the closet so that the bottom can be renewed from time to time without taking the apparatus to pieces.

Several forms of electric ovens are also in use. These require little attention and can be regulated to almost any desired temperature.

In order to dry the filter, place it in the oven upon a watch glass and near an open weighing beaker, bring the temperature to the desired point and keep it there, with the help of the thermo-regulator *T*, for $\frac{1}{2}$ to 1 hour. By means of tongs quickly place the filter in the weighing beaker, and allow the latter to remain in a desiccator filled with calcium chloride (Fig. 9), for exactly 1 hour. Cover the beaker, remove it from the desiccator, allow it to stand in the air near the balance for 20 minutes, and then weigh. Repeat this heating and weighing in exactly the same way until two consecutive weighings do not differ by more than 0.0002–3 g.

Collect the precipitate upon this weighed filter and after drying the filter in the funnel at 100° C remove the filter and its contents from the funnel and dry in exactly the same way as before.

The same result is much more simply and accurately accomplished by the use of the *Gooch crucible.*

As shown in Fig. 11, this is a crucible with a perforated bottom. The crucible is provided with an asbestos filter, weighed after drying at the prescribed temperature, then the precipitate is filtered off into the crucible, which is again dried and weighed. The use of these crucibles permits such accurate and rapid work that it is worth while to describe the method of using them more in detail.

Preparation of Asbestos Filters

Cut some long-fibered, soft asbestos, of the non-hydrated variety, into pieces $\frac{1}{2}$ cm long, and digest with concentrated hydrochloric acid upon the water-bath for

an hour. A good sample of asbestos will then be separated into very small fibers. Collect the mass in a funnel upon a filter plate, and wash with water until free from chloride. Such washed asbestos can now be purchased from dealers in chemicals.

For the preparation of a Gooch filter, shake some of the material with water in a flask, so that a thin suspension is formed. Stretch a piece of thin rubber tubing (Fig. 12) over a funnel and place the Gooch crucible T in the opening. The funnel should be large enough so that the crucible is suspended by the rubber without touching the sides of the funnel. Pour enough asbestos into the crucible to produce a layer of 1 to 2 mm thickness, place a small filter plate (Fig. 11, P) upon this layer, and pour a little more of the asbestos suspension into the crucible. Wash the felt with water until no asbestos fibers run through, and, in order to see them, pour the liquid into a small beaker. Usually such a filter is prepared and used with a gentle suction, but in many cases it filters more rapidly than paper without it.

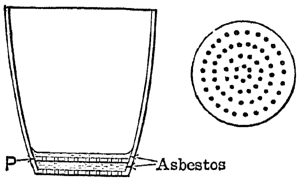


FIG. 11.

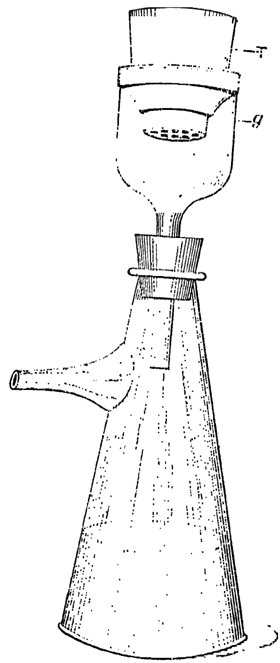


FIG. 12.

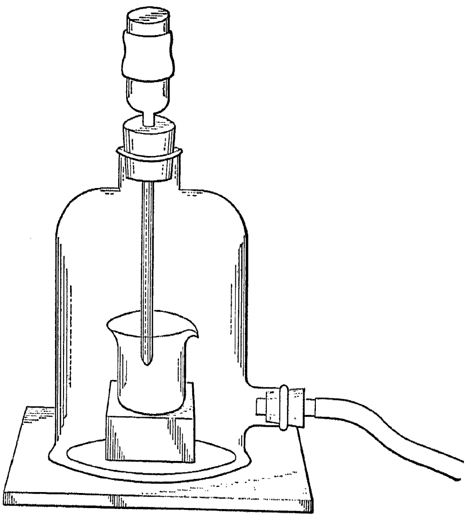


FIG. 13.

When suction is used it is sometimes desirable to filter into a beaker which is placed inside a bell jar arranged so that it can be evacuated (Fig. 13).

Dry the crucible at the proper temperature and afterwards weigh. Repeat the drying and weighing until a constant weight is obtained. It is advisable then to run about 500 ml more of water through the

crucible (in order to be sure that no asbestos fibers run through), and again dry and weigh. If the weight is constant, the crucible is ready for the filtration.

If it is desired to heat the precipitate to a higher temperature, the Gooch crucible should be heated inside another crucible or in an air-bath (Fig. 14) so that the gas flame does not play directly against the holes in the crucible. Electric ovens are also made which permit drying at temperatures up to 1000°, Fig. 15.

For many purposes it is preferable to use instead of the Gooch crucible a glass tube with an asbestos filter. This is particularly desirable when it is necessary to heat the precipitate in a gas stream.

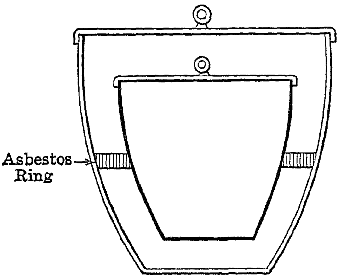


Fig. 14.

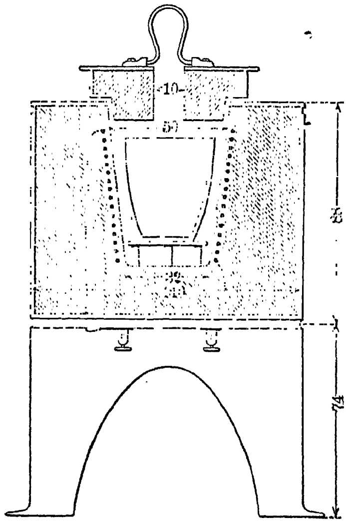


Fig. 15.

The so-called Munroe crucible,* in which the filtering medium consists of a porous felt of spongy platinum, is a modification of the Gooch crucible which permits rapid and accurate work. The felt is prepared by igniting a carefully dried layer of ammonium chloroplatinate, which has been poured over the bottom of a platinum Gooch crucible in the form of an alcoholic sludge while the crucible is held against several layers of filter paper. The felt can be shaped to the crucible during the ignition and subsequently burnished lightly with a glass rod of suitable form. If imperfections develop, the felt should be saturated again with chloroplatinic acid, the crucible slowly lowered into a moderately concentrated solution of ammonium chloride, washed with alcohol, dried, and ignited. On account of the high price of platinum, the

* C. E. Munroe, *J. Anal. Chem.*, **2**, 241; *Chem. News*, **58**, 101. See also W. O. Snelling, *J. Am. Chem. Soc.*, **31**, 456, and O. D. Swett, *ibid.*, **31**, 928. The last reference gives a table of suitable solvents for removing ignited precipitates from the Munroe crucible.

present tendency is to avoid its use as much as possible so that the Munroe crucible has never been popular. The Norton Company of Worcester, Massachusetts, make *Alundum* filtering crucibles which are very rapid but are rather slow to dry to constant weight at low temperatures. At Jena, Germany, filtering crucibles with sintered glass, porous bottoms are made with different degrees of porosity; they can replace the Gooch crucible to advantage for most purposes.

(b) THE PRECIPITATE IS IGNITED WET

Those precipitates which do not suffer any permanent change by the action of the products of combustion of the filter may be ignited wet. Allow the precipitate to drain as much as possible, and while still moist place the filter and precipitate in a crucible, with the paper folded so that the precipitate is not exposed and so that the moisture will be expelled through a layer of paper and not directly into the air. Place the crucible in an inclined position upon a triangle (Fig. 16),* with the cover inclined against the upper edge of the crucible and resting on the triangle. Direct the flame of the burner against the cover, which quickly dries the filter, then scorches it. Before it takes fire, move the flame to the back of the crucible and heat with a small flame until all the paper is consumed without taking fire, then slowly increase the temperature until finally the crucible is subjected to the whole heat of the burner, after which it can be heated over the blast lamp if necessary.

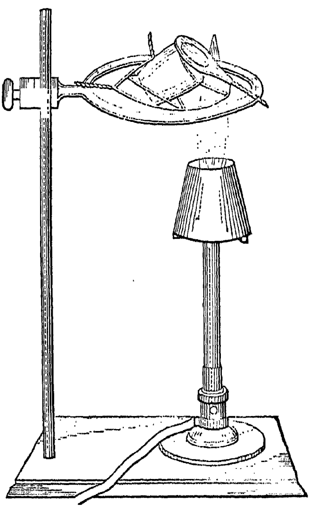


FIG. 16.

Always in igniting precipitates care should be taken to raise the temperature slowly. The object in keeping the flame near the mouth of the crucible at the start is to make sure that the contents of the crucible are dried from the outside. If the flame were placed at the base of the

* In Fig. 16, the inner triangle is platinum wire, the outer triangle is heavy iron wire. Triangles of fused silica or of nickel-chromium alloy are suitable, but since platinum alloys with iron, a hot crucible should never be placed in contact with iron wire.

crucible at the start, there would be more danger of loss by spattering.

As soon as the contents of the crucible are dry, the flame should be removed to the base of the crucible; and it is better to use a small flame near the crucible than to use a large flame with the crucible raised. Care should be taken not to let the paper take fire, except when the bulk of the precipitate has been removed from it and is ignited separately. When the paper burns rapidly in the crucible there is danger of a slight mechanical loss due to the rapid escape of the products of combustion.

Another procedure for igniting a wet precipitate is as follows: Place the crucible containing the precipitate and filter on an asbestos mat or wire gauze, and heat gently. Raise the temperature after all the water has been driven off; and when the paper has become charred, and not till then, transfer the crucible to a triangle and complete the ignition. By this method of drying the precipitate, four crucibles can be heated over one burner with a little supervision.

Too rapid heating of a paper filter may cause two other errors. Often the temperature is raised rapidly enough to fuse a little salt around the ash of the paper, and carbon inside such a fused coating is hard to burn because it is out of contact with the air. This is true, for example, of a silica precipitate, which is likely to retain a little adsorbed alkali salt. If the precipitate is heated rapidly a little carbon is likely to remain even after long ignition over the blast lamp.

Another serious error is sometimes caused by an undesirable reduction taking place. If the filter paper is smoked off slowly at a low temperature it is possible to heat magnesium ammonium phosphate in a platinum crucible without damage to the crucible or to heat ferric hydroxide without getting any magnetite formed.

With the magnesium ammonium phosphate it is quite likely that the reduction may be caused by ammonia as well as by carbon. The same principle holds, however, for if the ammonia is expelled slowly at a low temperature there is less danger of a harmful reduction than when the precipitate is decomposed rapidly by strong heating.

When the price of platinum was low, chemists were accustomed to use platinum vessels freely. Thus platinum evaporating dishes, platinum crucibles, platinum filtering cones, platinum spatulas, and heavy platinum wire were used in nearly every chemical laboratory. Since platinum has become more expensive, the chemist is learning how to get along without much of it. Glassware and porcelain are now made of better quality and can be used in chemical work without much contamination. Alloys such as palau or even nichrome are being used more and more. Most ignitions can be made in a porcelain or quartz crucible as well as in platinum. More time is required to cool these crucibles

after they have been heated, but the chemist learns to do something else during that time and in the end gets more work done by using a number of porcelain crucibles than he used to do with a few platinum ones.

Palau is the trade name of an alloy containing about 80 per cent of gold alloyed with palladium. It melts at 1370°, which is about 400° lower than the melting point of platinum. When heated to 1200° the loss in weight is less than that of platinum alloyed, as it is likely to be, with iridium. A crucible made of this material can be used satisfactorily in place of platinum except for fusions with potassium pyrosulfate.

Rhotanium is a trade name for another series of palladium-gold alloys, some of which contain rhodium. These alloys and their advantages have been described by Fahrenwald.*

Alundum† represents a refractory form of aluminum oxide. It does not fuse below 2050°. Crucibles can be obtained which are similar to porcelain crucibles, although they are not well glazed. Other Alundum crucibles are made more porous so that they can be used for filtering purposes instead of a Gooch or Munroe crucible. Some of them make very rapid filters, but it is hard to dry them and errors due to adsorption are much more serious than with a platinum or porcelain Gooch crucible.

The Properties and Care of Platinum

Platinum melts at 1770° but does not soften much until this temperature is nearly reached. It resists the action of all common acids except aqua regia and solutions containing chlorine. Long contact with acid ferric chloride solution is also injurious. It forms alloys with easily reducible metals and platinum crucibles are ruined when such alloys are formed. Long contact with hot carbon injures platinum, forming some carbide. For this reason a crucible should always be heated with an oxidizing flame; the flame should never show a luminous tip, and the top of the inner cone should be below the bottom of the heated platinum vessel.

Fusion with alkali hydroxides injures platinum, but the metal will stand fusion with alkali carbonate. Compounds of phosphorus are likely to be reduced by hot carbon, and the crucible is ruined when phosphide of platinum is formed.

Iridium has been used to harden platinum, but the alloy is less resistant to the action of reagents than pure platinum and the iridium is volatilized appreciably by heating over the blast lamp. Even good platinum ware is likely to become frosted by strong ignition but the surface crystals which cause the frosty appearance should be fine and evenly

* *J. Ind. Eng. Chem.*, **9**, 590 (1917).

† Saunders, *Trans. Am. Electrochem. Soc.*, **19**, 333 (1922).

distributed. A poor platinum alloy will often become covered with a whitish coating and with brown iron oxide stains. In buying platinum it is advisable to get *hammered* rather than *spun* ware, which is more likely to have surface cracks. It is well to specify that no distinct, uneven discoloration should result from heating, that treatment with acid should show no test for iron after heating 2 hours, that the loss on heating at 1100° should not exceed 0.2 mg per hour over a period of 4 hours, and that 5 per cent of rhodium instead of iridium should be present as hardening agent.

Handle platinum carefully and avoid bending. Use clean tongs for handling hot crucibles and do not let the tongs come in contact with melted flux.

To clean, use chromic acid for removing organic matter, hydrochloric or nitric acid singly (never mixed) to remove insoluble carbonates or metal oxides. Fuse with sodium carbonate or borax to remove silica or silicates and with alkali pyrosulfate to remove metals or oxides that resist the action of acids.

Never heat platinum with the inner cone of the Bunsen flame touching the vessel; this will cause brittleness.

Do not heat compounds of lead, tin, bismuth, arsenic, antimony, or zinc in platinum. Do not ignite sulfides in platinum, and avoid heating phosphorus compounds except with great care.

Do not attempt to remove fusions with knives, files, glass rods, or other hard tools. Use rubber-tipped rods or solvents.

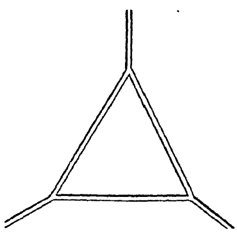


FIG. 17.

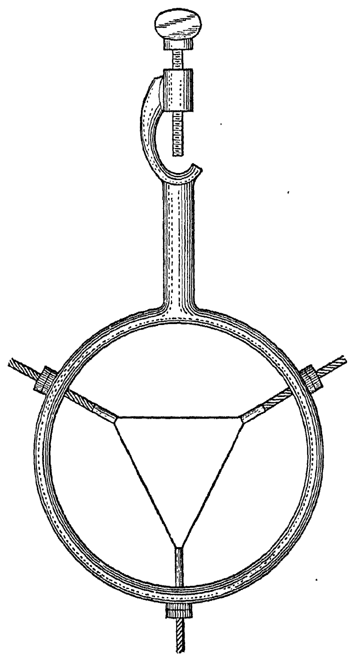


FIG. 18.

Polish dull surfaces with sea sand or very fine Carborundum* powder.

* "Carborundum" is the proprietary name of a special make of silicon carbide which is much used as an :

Triangles

For use with platinum crucibles, platinum triangles are desirable. Figures 17 and 18 represent two forms of these. The first is made of heavy platinum wire and is intended to rest on the ring of a lamp-stand. The second form is made so that it can be screwed on to the ring and thus kept in place.

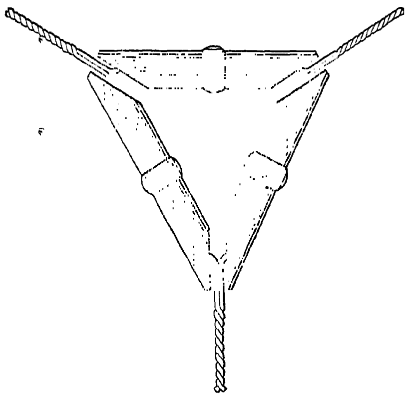


FIG. 19.

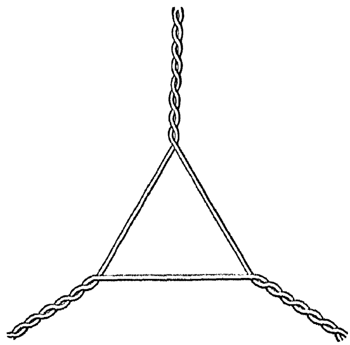


FIG. 20.

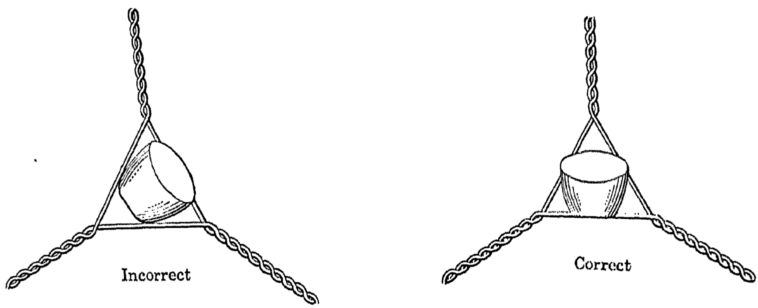


FIG. 21.

Figure 19 shows a clay triangle which can be used even for platinum crucibles, and Fig. 20 represents a less expensive nichrome triangle. This may be used with platinum if it is kept clean and no flux is spilled upon it, but there is some danger of staining the crucible with this kind of a triangle.

Triangles of fused quartz are also useful. Figure 21 shows the correct and incorrect ways of placing a crucible on a triangle in an inclined position.

Burners

Besides the ordinary Bunsen burners which are familiar to all, two other types deserve mention. The Tirrill burner is based upon the principle of the Bunsen burner but is an improvement in design. At the base of the burner the flow of gas is regulated by a screw which operates a needle valve, and the supply of air is regulated by screwing the tube of the burner up or down and thus allowing more air to enter through the holes at the base.

The Méker burner provides for a similar adjustment of gas and of air but the shape of the burner tube is different. The tube is narrowest near the base and widens out at the top. As a result the delivery of the gas under pressure into the inverted cone causes a greater reduction of pressure within the tube and a greater inflow of air than in other burners which do not operate with a blast. There is a more perfect mixing of the gas with air and a greater combustion of gas within a given space. At the top of the burner tube is fitted a nickel grid and the gas burns in a great many small flames with the tip of each inner reducing cone about 1 mm above the top of the burner. The many small flames unite to give a very hot and highly concentrated flame which is oxidizing in character except below the tips of the tiny flame cones. A crucible placed just a little above these tiny flames is heated nearly as hot as by a blast lamp.

Distilled Water

Various forms of stills are in common use. It is important that the vessel containing the boiling water should be so separated from the condenser that there is little danger of spray entering the latter. The boiler may be of any material, but the condensing worm and supply pipes should be of pure tin.

Distillation does not free water from carbon dioxide, oxygen, nitrogen, and ammonia, and supply tanks are likely to become slimy after a time. For water analysis and in any work involving the use of water free from nitrogenous compounds, it is necessary to distil the water a second time with permanganate in the boiler. The first and last runnings are then rejected.

Transfer of Liquids

In pouring out a reagent from a bottle never place the stopper on the work-bench. Pick up the stopper, hold it between the first two fingers of the right hand with the palm up, grasp the bottle with the same hand and the palm over the label, and pour from the bottle with

the label up so that there is no danger of any liquid falling upon the label. It is advisable to cover printed labels with thin coatings of gum sandarac dissolved in alcohol. In pouring liquids it is always advisable to pour against a glass rod so that none of the liquid is spilt. In removing the rod do not move it upward and scrape off a little liquid thereby. It is well to give the rod a slight downward motion on taking it away.

Reagents and Glassware

One of the greatest sources of trouble for the analytical chemist is the presence of impurities in reagents and the action of solutions upon glassware. It is desirable to use the purest possible reagents, but the chemist should always take care to test them. Even if the reagents are perfectly pure, they often become contaminated by solutions remaining in glass bottles. In every analysis, therefore, errors are likely to arise from impurities that were in the reagents or from glassware that has been somewhat dissolved. Solutions of strong acids and bases when kept for some time in bottles will always give a slight test for silica if sufficient reagent is taken for the test.

Today it is possible to buy glassware which is much less acted upon by reagents than that formerly used. Such glass is essentially a borosilicate of sodium, zinc, and aluminum.*

It is well sometimes to run through blank analyses to see if any weighable precipitates are obtained when the reagents alone are used in an analysis. Such analyses are often misleading because the precipitates are so small that they may be overlooked or they may be so fine that they need some other precipitate to adsorb them and prevent their passage through the filter.

THE EVAPORATION OF LIQUIDS

Liquids are usually evaporated upon the water-bath. In order to prevent anything from falling into the evaporating-dish it is well to cover it with an evaporation-funnel, as shown in Fig. 22.

The funnel is suspended above the dish by means of a porcelain fork fastened to the iron rod (covered with hard rubber) which is attached to the water-bath.

If the laboratory is provided with a glass-covered hood with a good draft the use of the funnel is unnecessary.

If, however, the hood is directly connected with the chimney it often happens that on a windy day a considerable amount of dust falls into

* In *Bur. Stand. Tech. Paper*, 107 (1908), the result of some tests on glassware are given. Since then several other good glasses have been developed.

the hood. To prevent this, the hood in the Zurich laboratory is provided with a glass roof, *aa*, Fig. 23, and about 15 cm below there is a second glass plate *bb* which does not quite touch the inner wall of the hood but is about 3 cm away from it throughout its whole length. Between the two plates there projects a clay pipe *R*, about 15 cm in diameter and about 5 cm above the inner edge of the lower glass plate, leading directly into the chimney *K*, in which there is a small gas flame (not shown in the illustration). Any dust, sand, etc., from the chimney falls upon the plate *bb*; none can get into the hood.

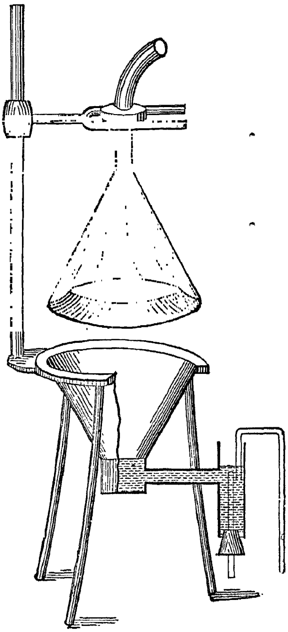


FIG. 22.

In the evaporation of liquids on the water-bath in weighed platinum crucibles or dishes, the platinum should not come in contact with copper or glass rings. As a rule, porcelain rings should be used. If the crucible is smaller than the ring, use is made of a truncated brass cone turned back at the base (Fig. 24*b*) and lined with thin platinum foil. This is suspended in the ring and the crucible placed within the cone (Fig. 24*a*).

During evaporation many substances have the property of "creeping" over the edge of the crucible or dish, often causing a slight loss of the substance; furthermore, there is often "bumping," so that in some cases the entire contents are thrown out of the crucible (cf. the determination of boric acid according to the method of Gooch). Both these phenomena can be readily prevented as follows:

Place the crucible, at the most not more than two-thirds filled with liquid, in a cylindrical tin or brass spiral *kk* (Fig. 25). The first two windings of the metallic spiral come into close contact with the sides of the crucible *above the liquid, while the remaining windings should not touch the crucible.* When steam is passed through the spiral the upper part of the crucible is warmed first, so that there is no spattering, and furthermore by keeping the upper edge hot during the whole of the evaporation all "creeping" of the substance is avoided. In this way it is possible to evaporate off alcohol rapidly without boiling the liquid.

If it is desired to evaporate high-boiling liquids, such as sulfuric acid, amyl alcohol, etc., either heat the crucible cautiously over the

free flame (continually moving it back and forth) or else place the crucible in an air-bath, which can be prepared in some such way as is represented by Fig. 26.

The Finkener tower, Fig. 27, is very useful for evaporating solutions to dryness and for heating the residue moderately as in silica determina-

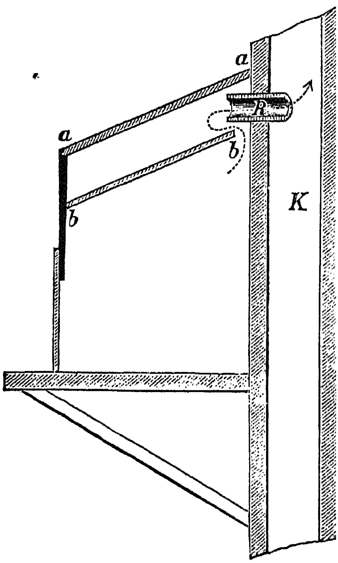


FIG. 23.

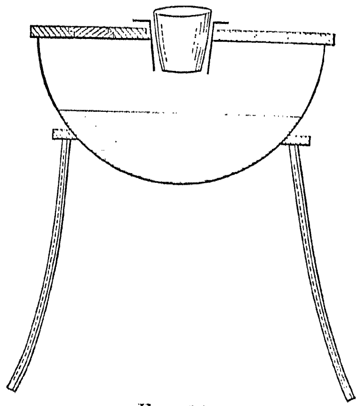
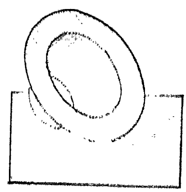


FIG. 24a.



tions. It consists of a rectangular, sheet metal box with several openings in which are placed pieces of wire gauze. The casserole is placed on top of the tower, and the heat is increased or diminished by removing or inserting layers of the wire gauze.

Drying Substances in Currents of Gases

Substances may be dried at a high temperature in a current of air or of carbon dioxide in a number of different ways. An oil-bath provided with a number of copper tubes (Fig. 28) may be used. Place the substance in a small " boat," put this in a glass tube and insert the tube into one of the copper tubes. Pass the gas through one or more of the empty tubes (so as to warm it), and then through the tube containing the substance.

If it is desired to evaporate off a liquid in a flask and to ignite the residue at a given temperature it is well to proceed as follows:

Place the solution in an open Erlenmeyer flask *K*, Fig. 29*a*, and evaporate as far as possible over the free flame. Then place the flask

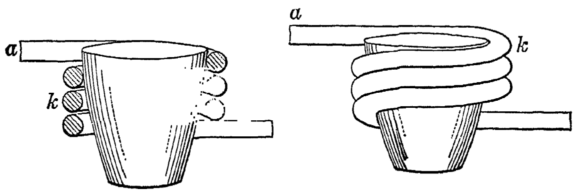


FIG. 25.

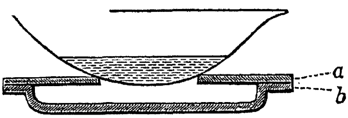


FIG. 26.
a = asbestos ring.
b = asbestos plate.

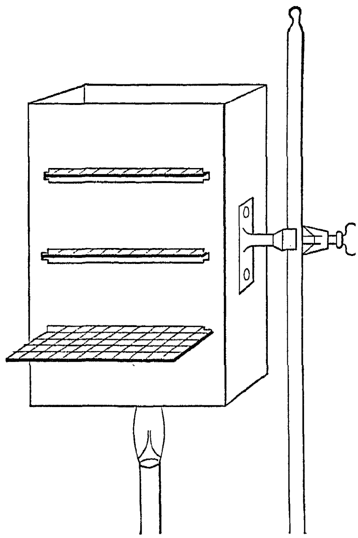


FIG. 27.

in a metal beaker suspended in an oil-bath (Fig. 29*a*), and aspirate dry air through the spiral copper tube *kk* as shown in the illustration. Figure 29*b* shows the separate parts of the apparatus.

PREPARATION OF THE SUBSTANCE FOR ANALYSIS

It is very difficult to give general rules for the preparation of substances for analysis, for it is necessary to proceed differently in different cases. If it is desired to determine the atomic composition of a substance, it is necessary to choose pure material for the analysis. Although this sounds so simple it is often one of the most difficult con-

ditions to fulfill. Many substances are hygroscopic and absorb moisture from the air, which can be removed by heating the substance or by simply allowing it to stand in a desiccator over calcium chloride, provided the substance itself undergoes no change by this treatment.

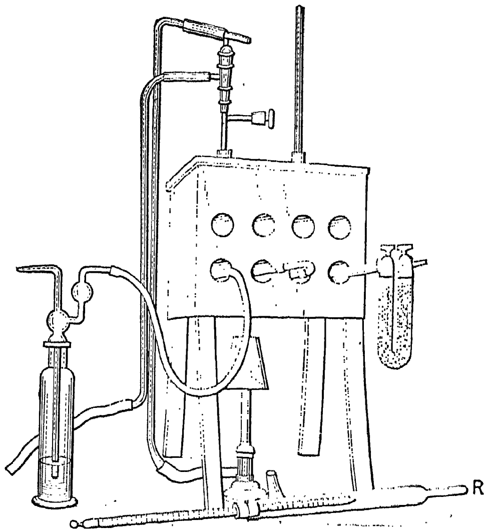


FIG. 28.

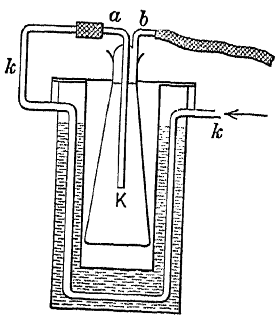


FIG. 29a.

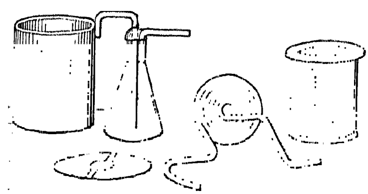


FIG. 29b.

Many substances containing water of crystallization cannot even be dried in a desiccator, but must be analyzed air-dry. In all cases it is necessary to determine whether the substance to be analyzed possesses a constant weight.

Many commercial salts are prepared pure and can be analyzed directly; in most cases, however, they have stood for some time in the

air and have been handled somewhat, so that they are not so pure as when freshly prepared. Consequently, if it is desired to test the accuracy of an analytical process, the purity of a commercial sample should never be taken for granted. If the substance is soluble in water it can be purified by recrystallization.

Dissolve 10 or 15 g of the commercial salt in the least possible amount of hot water (it is best to use not quite enough water to dissolve the substance *completely*), and pour the hot solution through a plaited filter contained in a funnel with the stem broken off (Fig. 30). This serves to remove all dust or other insoluble impurity. Catch the filtrate in an evaporating-dish and cool it rapidly, while stirring constantly, by placing the dish in a larger one containing cold water.

By means of the rapid cooling and constant stirring, the salt is obtained in the form of a crystalline powder.* Filter off the crystals and

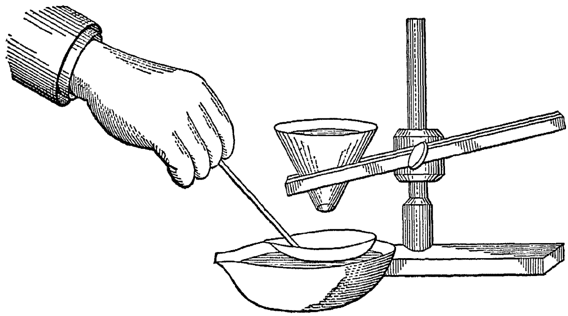


FIG. 30.

drain them by suction. A perforated porcelain plate covered with filter paper may be used in the funnel, or an ordinary filter may be used placed in a perforated filter cone or in a small hardened paper, to prevent tearing the paper by suction. Test the purity of the substance qualitatively by means of some suitable reaction. If it is still not quite pure, repeat the same process of recrystallization until the presence of no impurity can be detected.

Place the pure, moist crystals upon a layer of several thicknesses of clean filter paper, cover with another sheet of filter paper, and allow the crystals to stand for 12 hours at the ordinary temperature. Then weigh out 1 or 2 g of the substance upon a tared watch glass, place it

* Large crystals would be obtained by allowing the solution to cool slowly, but they are undesirable, as they usually contain more enclosed mother-liquor than do the smaller crystals. Most water-soluble salts are much more soluble in hot water than in cold water.

upon a dry glass plate, cover loosely with another watch glass, and allow it to stand for several hours more. If the substance shows no change in weight it is ready for analysis. Otherwise it must be dried in the air until it no longer shows a change in weight. It is permissible to dry in a desiccator only those substances which will not lose water of crystallization. Deliquescent substances, of course, should not be allowed to remain exposed to the air for very long. Such substances must be quickly dried upon a porous plate and transferred as soon as possible to a flask provided with a closely fitting, ground-glass stopper.

For *technical analyses*, the purpose being to determine the cost or selling price of an article or to control its manufacture, the substance must be analyzed *as it is*. The sample should represent as far as possible the average composition of the product.

The selection and preparation of representative samples for analysis are matters of so great importance that they have been discussed in more than 1200 papers* written since 1892. The quantity of material from which the sample for analysis should be taken varies with the nature of the material. If it is homogeneous it is merely a matter of grinding a portion until it is of suitable fineness.

The Influence of Fine Grinding on Composition

The rate at which a substance dissolves increases as the amount of surface exposed to the solvent is increased, and for this reason solid substances always dissolve more quickly when reduced to a fine powder. Moreover, when a material undergoes chemical attack, an insoluble substance is often formed and, during the process of solution, the insoluble substance may form a protective coating over particles of material that have not been acted upon. This danger is diminished if the material is in the form of a fine powder. For these reasons the chemist usually prefers to grind a solid substance to an impalpable condition before attempting to analyze it.

This practice, though desirable in most cases and absolutely necessary in others, is accompanied by certain disadvantages. If the material is hard there is always some contamination from the material of which the grinding apparatus is constructed. Thus when the sample is ground in a steel mortar or in a steel ball-mill, it will be contaminated with a little iron, and if ground in an agate mortar with a little silica.† Again,

* Cf. W. J. Sharwood and M. M. Bernewitz, *Bibliography of the Literature on Sampling*, Bureau of Mines Publication. Serial No. 2336.

† Hempel (*Z. angew. Chem.*, **1901**, 843) found that an agate mortar and pestle lost 0.052 g in grinding 10 g of glass to a fine powder. E. T. Allen found a loss of 0.145 g of agate in grinding 200 g of quartz.

if the sample readily undergoes slight decomposition, such a chemical change is likely to take place during the operation of grinding. In this way the determination of moisture, of ferrous iron, and of sulfur may be influenced very appreciably.

A number of investigators have pointed out the effect of grinding upon the moisture content of a sample. If the sample is practically dry, it is likely to absorb considerable moisture when dried in the air. Thus Hillebrand* found that a piece of unglazed porcelain contained no moisture originally, but showed 0.62 per cent of water when ground. If the substance is very hygroscopic, this danger becomes greater. On the other hand, grinding often causes loss of moisture. This is notably true of substances containing water of crystallization or superficial moisture. Thus grinding can easily reduce the moisture content of a sample of gypsum from 20 to 5 per cent, and a sample of coal may show several per cent of moisture when large lumps of it are tested and very little moisture after it is reduced to a fine powder.

The heat produced by grinding may not only serve to expel moisture from the sample, but it may even cause chemical change. Thus Mauzelius† has shown, and the experiment has been repeated by Hillebrand,‡ that the ferrous iron content of a rock becomes smaller on account of grinding it to a fine powder. It has also been found that some sulfur may be lost by long grinding of a sample of pyrite.

The effect of grinding, therefore, accounts for many divergent results obtained by different chemists who have analyzed the same original material.

Sampling a Shipment. — To prepare a representative sample from a large mass of material, such as a shipment of ore or of coal, special precautions are necessary. It is never safe to take samples from the top of a large pile of material, but portions should be selected from all parts. The easiest way to do this is in the loading or unloading of the shipment, taking out portions at regular intervals either by a shovel, trowel, or mechanical sampler. In sampling coal, the United States government § takes, as a rule, 1000 pounds from each shipment of 500 tons or less. The size to which ore must be crushed for sampling depends ¶ on (1) the weight of material given to the chemist from the shipment, (2) the relative ratio of the richest mineral value and the average

* *The Analysis of Silicate and Carbonate Rocks*, Bull. 700, U. S. Geol. Survey.

† *Sveriges Geol. Undersökning*, Årsbok 1 (1907).

‡ *J. Am. Chem. Soc.*, **30**, 1120 (1908).

§ G. S. Pope, *Methods of Sampling Delivered Coal*, Bur. of Mines, Bull. 116.

¶ D. W. Brunton, "The Theory and Practice of Ore Sampling," *Trans. Am. Inst. Min. Eng.*, **25**, 827 (1895).

value of the ore, (3) the density of the richest material, and (4) the number of particles of the richest mineral. The more " spotty " the ore the larger must be the original weight selected. The results of Brunton's work show that it is necessary to crush the sample before " cutting it down " and advisable after each " cutting " to crush it still finer.

Crushing the Sample. — After enough material has been taken from a shipment to guarantee a representative sample, the next operation is to crush it so that the largest particle is not larger than a certain definite size. Thus with a sample of coal weighing 1000 pounds, it is all broken up so that the diameter of the largest piece is not over one inch. This may be done by a mechanical grinder* or by hand with an iron tamping bar or sledge. In mineral analysis, where smaller samples are usually taken, samples are often broken up by pounding on a hardened steel surface with a hardened hammer of the best tool steel.†

Mixing and Coning. — To mix the sample, it is customary to shovel it into a conical pile. Each shovelful should fall upon the apex of the cone, the material should be thrown so that the cone is not pushed away from its original position, and the shoveler should walk around the cone as he shovels. This serves to bring the finer material near the center of the pile, and the coarser pieces run down the sides. Of the first cone usually one half is rejected. This can be done by shoveling away the cone from the bottom, while walking around the cone, and rejecting every other shovelful. Or the cone may be flattened and quartered.

Quartering. — The top of the cone is flattened out and divided into quarters. Opposite quarters are taken for the next crushing.

The mixing, coning, quartering, and crushing should continue until finally a sample of 100–200 g is obtained. When the samples are small enough, the mixing is best done on a sheet of glazed paper, rubber, or oilcloth. A corner of the sheet is lifted and drawn across, low down, in such a way that the material is made to roll over and over and does not merely slide along. The sample should be rolled back and forth along each diagonal for 100 times or more. Then the sample may be spread out into squares and a little taken from each square. In weighing out an ore it is always well to mix it by rolling back and

* W. F. Hillebrand, *The Analysis of Silicate and Carbonate Rocks*, U. S. Geol. Survey, Bull. 700.

† Mechanical grinders should be made of specially hardened steel and should be built so that they can be kept clean easily. For laboratory grinding, a modified McKenna ore grinder has been recommended by Hillebrand. (*Bull.* 700, U. S. Geol. Survey.) A picture of this grinder will be shown later. See Analysis of Silicates.

forth unless it is extremely fine, when it is not likely to segregate on standing. Segregation takes place when particles are of different sizes and densities.

If in the sifting of an ore, metallic particles are left on the screen, it is necessary to analyze these particles separately and make a proper allowance in the final calculation. It is necessary then to know the weight of the entire sample and the weight of metal that does not pass through the screen.

In sifting samples, wire screens are commonly used, but inasmuch as a little metal is introduced into the sample, it is better to use silk bolting-cloth.

The **cutting,** or **dividing,** at the several stages of the sampling process is best done by mechanical means. Some machines, of the riffle type, constantly deflect a part of the material that passes through them. Others, which for some purposes are more desirable, change the direction of the fall of the ore at regular intervals. Buckets are constructed so that, as ore is poured into them, half of it is retained and half rejected. Split shovels, consisting of a series of parallel troughs with equally wide spaces between them, are made of various sizes. The ore retained by the shovel, or that which passes through, may be taken for the sample. In using such shovels, of which the smallest size is useful for weighing out samples that are not perfectly homogeneous, allow a thin stream of ore to fall back and forth over the riffle. The distance between riffles should be at least three times the diameter of the largest particles of ore.

In sampling metals and alloys it is necessary to remember that they are seldom homogeneous. During solidification the part that solidifies last is usually different from that which first separates on cooling. As a rule, the outside of an ingot solidifies first and some of the impurities are likely to be concentrated or segregated in the interior. In the case of a steel rail, microscopic examination often shows that the head, the foot, and the web are not exactly the same. The sample used for analysis should consist of borings taken from all over the rail, or, better still, it should be obtained by planing over the entire cross-section. A macroscopic* survey of the entire cross-section after it has been treated with a suitable etching agent, such as an 8 per cent solution of cupric ammonium chloride or a 6 per cent solution of iodine in alcohol for steel specimens, will often show where segregation has taken place. When metals break under strain, the crack usually starts at some place

* Magnifications of less than 10 diameters are often classed as macroscopic, although strictly speaking, they are not included in an exact definition of the term.

where the material is defective, usually owing to a little enclosed slag. The analysis of the entire material will often fail to indicate a defective material, and the cause of the fracture can be shown only as a result of metallographic examination of polished specimens under the microscope and the chemical analysis of portions where segregation has been revealed by the microscope.*

* Cf. Hall and Williams, *Chemical and Metallographic Examination of Iron, Steel and Brass.*

PART I

GRAVIMETRIC ANALYSIS

A. GRAVIMETRIC DETERMINATION OF THE METALS (CATIONS)

METALS OF GROUP V

POTASSIUM, SODIUM, LITHIUM, AMMONIUM, AND MAGNESIUM

POTASSIUM, K. At. Wt. 39.096

Forms:* KCl, K_2SO_4, K_2PtCl_6, and $KClO_4$

1. The Determination as Chloride

This compound is chosen for the determination of potassium when it is already present as such, or if the salt to be analyzed may be changed to chloride by evaporation with hydrochloric acid. If the potassium is present as sulfate it may be transformed to chloride by precipitation *of the sulfate* with barium chloride (see Silicate Analysis); if it is present as the phosphate, the phosphoric acid may be precipitated as basic ferric phosphate (Vol. I); or, finally, if it is present as chromate the $CrO_4^{=}$ ions may be reduced to chromic ions by evaporation with hydrochloric acid and alcohol and then precipitated by ammonia and filtered off.

In almost all these cases it is a question of separating the potassium chloride from the aqueous solution and usually of separating it from ammonium chloride as well.

Procedure. — Evaporate the solution to dryness on the water-bath in a platinum or thin *porcelain* dish, stirring frequently as soon as the salt begins to separate out in order to hasten the evaporation of the enclosed water. In spite of long-continued heating and continual stirring, however, it is not possible to expel all the water enclosed within the crystals; to accomplish this, heat the covered dish in a hot closet or drying-oven for at least an hour at 130–150°. Then remove the watch glass and heat carefully over a small flame until no more vapors are evolved, taking care not to heat too strongly because of the danger of volatilizing some potassium chloride. Usually there is a little carbon in the residue, due perhaps to a little pyridine in ammonia used in the analysis. Treat the residue with a little water and filter through a

* Under this heading will be given in every case the symbols of the compounds suitable for the determination of the element in question.

small filter into a weighed crucible or dish, preferably of platinum. Add a few drops of hydrochloric acid, carefully evaporate to dryness, and remove the last traces of moisture by drying and heating as before. Cool, weigh, and repeat the heating until a constant weight is obtained.

In all the methods of gravimetric analysis described in this book it will be understood that when a crucible is "heated" and "weighed" the operations should be repeated to see if the weight is constant. As a general rule, a weight may be regarded as constant when it agrees within 0.3 mg with the previous weight or when the difference is less than one-thousandth part of the entire weight.

The above method of analysis is capable of yielding exact results and is suitable to give beginners in quantitative analysis.

Example. — Determination of Potassium in Potassium Bichromate.

Dissolve 0.5–0.6 g of the powdered salt (weighed to the nearest tenth of a milligram) in a 300-ml porcelain casserole. Add 10 ml of concentrated hydrochloric acid and 5 ml of alcohol. Cover the dish with a watch glass and heat on the water-bath until all the bichromate is changed to chromic salt as shown by the emerald green color of the solution. Remove the watch glass and rinse off the under surface into the casserole to remove any salt that may have spattered upon it during the evolution of chlorine. Evaporate to dryness; add 2 ml of concentrated hydrochloric acid and 200 ml of water. Heat just to the boiling point, and to the hot solution add enough dilute ammonia to precipitate all the chromium but avoid an excess. Filter and wash the chromic hydroxide precipitate until a little of the filtrate gives no test for chloride with silver nitrate solution.

Evaporate the filtrate and weigh the residual potassium chloride taking all the precautions described on the previous page. If a little chromic hydroxide is deposited during the evaporation, it must be filtered off and the precipitate washed with hot water until free from chloride.

From the weight of potassium chloride, compute (*a*) the percentage of K, (*b*) the percentage of K_2O, and (*c*) the percentage purity of the sample. The computation is explained in the Appendix. It is advisable to carry out all analyses in duplicate. The results should agree within two parts in one thousand* and should not be far from the

* Considerable misunderstanding often arises with regard to the meaning of a "check within two parts in one thousand or within 0.2 per cent." The agreement should always refer to the value itself and not to the percentage of the weight of sample. Thus if two analyses of $K_2Cr_2O_7$ give values 31.95 and 32.01 per cent K_2O, the check is two parts in one thousand or 0.2 per cent of the value found.

truth, although a little potassium is adsorbed by the chromic hydroxide precipitate.

2. Determination of Potassium as Potassium Sulfate

This method is chosen when the potassium is already present in solution as the sulfate, or when it is in such a form that it can be readily changed to sulfate by evaporation with sulfuric acid; it is most frequently used for determining the amount of potassium in combination with organic acids.

Since the sulfate of potassium is much less volatile than the chloride, it is advisable to choose this method if no other metal is present. On the other hand, when it is necessary to separate potassium from sodium, it is preferable to have the potassium in the form of the chloride.

Example. — Determination of Potassium in Potassium Bichromate. Weigh 0.5 g of the powdered salt into a 300-ml porcelain evaporating-dish, and treat with 20 ml of a freshly prepared, saturated, aqueous solution of sulfur dioxide* and 5 ml of 2 N sulfuric acid. Cover the dish with a watch glass and heat on the water-bath until there is no more evolution of gas. Then remove the cover glass, rinse it off, and evaporate the solution almost to dryness. Add 200 ml of water and precipitate the chromium as in Method 1. Filter off the precipitate and wash it with hot water until a little of the filtrate gives no test for sulfate with barium chloride. Evaporate the filtrate containing potassium and ammonium salts to dryness, heat in the hot closet and expel the ammonium salts as described in Method 1. In this case, however, there is less danger of vaporizing the potassium salt. After weighing the cold dish or crucible, add a small piece of solid ammonium carbonate, about the size of a pea, to decompose any $K_2S_2O_7$, and heat again until a constant weight is obtained.

From the weight of K_2SO_4, compute the percentages of K, K_2O, and of $K_2Cr_2O_7$ in the original salt.† There is a slight adsorption of potassium by the chromic hydroxide precipitate.

* The solution of sulfur dioxide may be prepared as follows: Take 150 ml of saturated $NaHSO_3$ solution in a 300-ml Erlenmeyer flask and slowly add concentrated sulfuric acid from a drop-funnel. Pass the evolved SO_2 gas into a small wash-bottle containing water and then into another wash-bottle containing distilled water, which is kept cool by placing it in a larger vessel filled with cold water. When the evolution of the SO_2 begins to slacken, it can be accelerated by gentle warming.

† In quantitative analysis it is customary to report results in the form of the most representative oxide. This method of representation is based upon the dualistic theory. There are several reasons why the analytical chemist continues to express his results in these terms. (1) It furnishes the most convenient way of properly

To determine the quantity of potassium in an organic salt, treat a known weight of the salt in a large, weighed crucible with a little concentrated sulfuric acid. Heat exactly as in the case of igniting a moist precipitate (see p. 38) placing the crucible in an inclined position and directing the flame against the cover of the crucible. Thick, white fumes of sulfuric acid are soon evolved; as soon as these begin to diminish in quantity gradually move the flame toward the base of the crucible, and finally heat to dull redness until no more vapors are given off. The mass remaining in the crucible now consists of K_2SO_4 and $K_2S_2O_7$. The latter compound can be converted by stronger ignition into K_2SO_4 with loss of SO_3, but as this procedure involves a slight loss of potassium it is preferable to add a little solid ammonium carbonate, by means of which the excess of sulfuric acid is converted into ammonium sulfate, which is readily volatile and can be decomposed at a much lower temperature.

3. Determination of Potassium as K_2PtCl_6 and as $KClO_4$

These determinations are employed only when it is necessary to effect a separation of potassium from sodium. They will be discussed under the Separation of Potassium from Sodium.

SODIUM, Na. At. Wt. 22.997

Sodium, like potassium, is determined in the form of its chloride and of its sulfate, and the same precautions which were discussed under

apportioning the element oxygen which is practically never determined directly when present in a compound. Thus in the analysis of bichromate it is more satisfactory to report the percentage K_2O and percentage CrO_3 than it is to subtract the K and Cr contents from 100 and call the difference oxygen, or to report the Cr as Cr_2O_7 and thus arbitrarily make the accuracy of the chromium determination the only factor governing the oxygen content. (2) When reported in this way, the analysis of salts of all oxygen acids should add up to 100 per cent and this furnishes a fairly satisfactory check on all the determinations made. If a salt of a binary acid is present, *e.g.*, a sulfide or halide, the results should add up to more than 100 per cent if the metal of the sulfide or halide is reported as oxide. In such cases, it is customary to deduct a weight of oxygen equivalent to the weight of sulfide or halide. Thus mineral analyses made in the laboratories of the U. S. Geological Survey often close with the statement "Less oxygen for fluoride, sulfide, etc." (3) The statement that a substance contains K_2O and CrO_3 does not mean that these constituents are present in an uncombined condition but it shows that the chromium is present as chromate or dichromate and not as chromic salt. The statement that a substance contains FeO and SO_3 means that the substance contains iron as a ferrous salt and sulfur as a sulfate. (4) The continuance of this system of reporting analyses makes it easy to compare results with those made fifty years ago even although the dualistic theory has been abandoned.

potassium hold for sodium. It may be mentioned, however, that NaCl and Na_2SO_4 are more difficultly fusible and less volatile than the corresponding potassium compounds.

Separation of Potassium from Sodium

The solution should contain salts of no other metals with the exception of ammonium salts. In order to separate the sodium and potassium they should both be present as chlorides, the combined weight of which is first ascertained. The mixture is then dissolved and the potassium precipitated out either as chloroplatinate or as perchlorate. From the weight of the precipitate, the corresponding amount of potassium chloride can be calculated, which value is deducted from the weight of the combined chlorides; this gives the weight of sodium chloride originally present. The sodium, therefore, is determined by difference. It is important that no ammonium salt be present as otherwise insoluble ammonium salts will precipitate with the potassium.

Rubidium and cesium chloroplatinates and perchlorates are even less soluble than the corresponding potassium salts. If, therefore, these rare alkali cations are present in the solution when the separation of sodium from potassium is made, they will be precipitated together with the potassium.

A. Separation of the Potassium as K_2PtCl_6

Principle. — Potassium chloroplatinate is practically insoluble in absolute alcohol, whereas the corresponding sodium salt is soluble. On the other hand, sodium chloride is insoluble in absolute alcohol, so that it is necessary to convert both the potassium and the sodium into chloroplatinates, as otherwise the potassium chloroplatinate obtained will be contaminated with sodium chloride and too high a value will be found for the amount of potassium present.

Procedure. — Dissolve the weighed chlorides (0.2 g or less) with a little water in a small porcelain dish. Add enough chloroplatinic acid to combine with all the alkali present, assuming, to be on the safe side, that the sample is all sodium chloride. Of the usual reagent, containing 10 g of dissolved platinum in 100 ml, 1.7 ml should be used for each 0.1 g of chloride. Enough water should be present to dissolve any precipitate of K_2PtCl_6 when the contents of the dish are heated on the water-bath.

Evaporate the solution nearly to dryness on a water-bath.* Stop evaporating when the contents of the dish solidify on cooling. Drench

* A convenient bath is obtained by placing the dish on a beaker half filled with water, which is kept just below the boiling point by a flame beneath the beaker.

the residue with a little 80 per cent ethyl alcohol and break up the mass of crystals into a fine powder by means of a stirring-rod or a platinum spatula. Decant the liquid through a filter moistened with alcohol, and repeat the treatment of the residue with alcohol until the filtrate runs through completely colorless and the salt remaining in the dish assumes a pure, gold-yellow color without any orange-colored particles being present ($Na_2PtCl_6 \cdot 6H_2O$).

Try not to get much if any of the precipitate upon the filter. Dry the dish and filter a few minutes to remove the alcohol, transfer the precipitate to a weighed crucible or very small dish and wash out the original dish with several small portions of hot water poured through the above-mentioned filter. Evaporate to dryness on the steam-bath and heat for 30 minutes in an air-bath at 135°, with the crucible or dish covered to avoid loss by decrepitation. Cool and weigh. From the weight of the K_2PtCl_6, compute the corresponding weight of KCl.

Remark. — Treadwell recommends the use of absolute alcohol because it has been claimed that anhydrous sodium chloroplatinate is more soluble in absolute alcohol.* This claim has been disputed.† Treadwell also recommends the use of the empirical factor 0.3056 for computing the KCl content, instead of the theoretical value

$$\frac{2\,KCl}{K_2PtCl_6} -$$

but according to the directions given here with drying at 135° instead of 160° and with the 80 per cent alcohol, the true factor seems more suitable. Results about 0.3 per cent too high have been explained on the assumption that the precipitate contains besides K_2PtCl_6 a little $KHPtCl_5OH$.

Determination of Sodium. — As already stated (p. 59), the sodium is usually determined indirectly. From the weight of NaCl + KCl obtained before treatment with H_2PtCl_6 in the determination of potassium, deduct the weight of KCl that is equivalent to the weight of the K_2PtCl_6 precipitate, and the difference gives the weight of the NaCl. This assumes that sodium and potassium are the only alkalies present.

To obtain the weight of NaCl directly, transfer the filtrate from the K_2PtCl_6 precipitate to a 100-ml flask and evaporate off most of the alcohol. Dilute if necessary, and expel all air from the flask by introducing a stream of pure hydrogen gas. Continue introducing the gas, while keeping the solution warm by immersing the flask in warm water, until all the platinum is precipitated as finely divided metal. Replace the hydrogen with an inert gas and filter off the platinum. Wash the precipitate with water. Evaporate the filtrate until the volume is small enough to permit the transfer to a weighed crucible. Then evaporate in an air-bath. Toward the last, cool, add some concentrated HCl to cause fine crystals of NaCl to form, and again

* Cf. Fresenius, *Z. anal. Chem.*, **1882**, p. 234. Also F. Dupré, *Die Bestimmung des Kaliums als Kaliumplatinchlorid*, Inaugural Dissert., Halle, 1893. Also W. Dittmar and McArthur, *J. Soc. Chem. Ind.*, 6, 799, and *Ber.*, **1888**, Ref. 412.

† Cf. W. F. Hillebrand, *Bull.* 700, *U. S. Geological Survey*, p. 211. The method here described corresponds to that recommended by Hillebrand.

heat carefully in the air-bath until the residue of NaCl is perfectly dry and there is no audible decrepitation when the crucible is heated carefully with a free flame. Cool in a desiccator and weigh.

Modification of Chloroplatinate Method

Instead of weighing the K_2PtCl_6, the dry precipitate may be heated in a stream of hydrogen, when HCl and H_2O will be given off and a mixture of platinum and potassium chloride will remain behind.

1. If the evolved hydrochloric acid is determined and from this the weight of potassium chloride is computed the result will be too low because less hydrochloric acid is evolved than corresponds to the equation:

$$K_2PtCl_6 + 2\,H_2 = 4\,HCl + Pt + 2\,KCl$$

2. If the mixture of platinum and potassium chloride remaining in the dish is weighed and from this the amount of potassium chloride is calculated, too low a result will be obtained.

3. Finally, if the mixture of platinum and potassium chloride is treated with water and, on the one hand, the weight of the platinum remaining undissolved and, on the other hand, the weight of the potassium chloride which goes into solution (by evaporating the solution and weighing the residue) is determined, then the amount of potassium chloride calculated from the weight of the platinum again gives a result which is too low; but the amount of potassium chloride found in the aqueous solution corresponds to the amount of potassium chloride originally present.

Inasmuch as the precipitate of potassium chloroplatinate possesses a constant composition it is possible to determine experimentally by working with pure material the exact ratio which exists between (*a*) the amount of hydrochloric acid evolved, (*b*) the mixture of potassium chloride and of platinum remaining after the ignition, (*c*) the weight of platinum remaining undissolved after treatment of the residue with water and the amount of potassium chloride originally present. According to Dupré, if the amount of platinum determined according to (*c*) is multiplied by the factor 0.7614 the true amount of potassium chloride will be obtained.

Determination of a Little Potassium in the Presence of Much Sodium*

Weigh out into 150-ml beakers samples of about 1.5 g, dissolve the salt in 25 ml of water, and add 5 or 6 ml of 60 per cent $HClO_4$, *d.* 1.54,

* G. F. Smith and J. L. Gring, *J. Am. Chem. Soc.*, **55**, 3957 (1933).

or 8 to 9 ml of 6 N $HClO_4$. Evaporate to dryness on the hot plate and expel any acid on the beaker walls by brushing lightly with a free flame. Cool, wash down the walls of the beaker with a little water, and repeat the evaporation in order to get a residue free from excess $HClO_4$. Digest the dry residue with 95 ml of 95 per cent ethyl alcohol, heating nearly to the boiling point of the alcohol. Now add a hot solution of 0.2 g chloroplatinic acid in 5 ml of 95 per cent alcohol, and after a few minutes' vigorous stirring, cool to 0°. After the solution has stood an hour or longer at this temperature, filter through a sintered glass or quartz filtering crucible, wash once with 95 per cent alcohol and finally with absolute alcohol until free from $NaClO_4$, dry at 110°, and weigh. The precipitate will stand heating to 350° without decomposition.

This method is economical in the use of the expensive chloroplatinic acid and from a solution of $KClO_4$ and $NaClO_4$ the conditions are favorable for forming a pure precipitate of K_2PtCl_6 even when very little potassium and much sodium are present.

B. Separation of Potassium from Sodium by the Perchlorate Method*

Principle. — This separation depends upon the insolubility of potassium perchlorate and the solubility of sodium perchlorate in 97 per cent alcohol. Ammonium salts and sulfates must not be present on account of the difficult solubility of ammonium perchlorate and of sodium sulfate in alcohol, but a little phosphate does no harm, as both sodium perchlorate and phosphoric acid are soluble in alcohol.

Many experiments by the agricultural chemists of the United States show that the method is nearly, if not quite, as accurate as the chloroplatinate method. It requires a little more attention to details. Since 1914 the price of platinum has been so high that it has interfered seriously with its use in the chemical laboratory.

In the analysis of fertilizers, the Association of Official Agricultural Chemists recommends placing 2.5 g of sample on a 12.5-cm filter paper in a funnel and dissolving the soluble salts by treating with small portions of hot water until about 200 ml of filtrate are obtained. Then 5 ml of concentrated hydrochloric acid are added and the sulfate precipitated. The solution is diluted to exactly 250 ml in a calibrated flask and, after mixing thoroughly, a little of the solution is filtered through a dry filter and exactly 50 ml of filtrate taken for the rest of the analysis.

By taking a fairly large portion for analysis and then using an aliquot part, a more representative analysis is obtained if the sample is not perfectly uniform. It is assumed that the actual volume of precipitate can be neglected and no attention is paid to adsorption of solute by the precipitate or by the filter paper. Such effects

* Schlösing-Wense, *Z. angew. Chem.*, **4**, 691; **5**, 233; **6**, 68; *Landw. Ver. Sta.*, **59**, 313; **67**, 145; *J. Am. Chem. Soc.*, **36**, 2085. Cf. also *U. S. Chemical Bulletin* 152; Baxter and Kobayashi, *J. Am. Chem. Soc.*, **39**, 249 (1917); **42**, 735 (1920); Davis, *J. Agri. Sci.*, **5**, 52 (1912); Gooch and Blake, *Am. J. Sci.*, **44**, 381 (1917); T. D. Jarrell, *J. Assoc. Official Agri. Chemistry*, **4**, 76–7 (1920–21); H. H. Willard, *J. Am. Chem. Soc.*, **34**, 1480 (1912); H. H. Willard and G. F. Smith, *ibid.*, **44**, 2816 (1922); **45**, 293 (1923); G. F. Smith, *ibid.*, **47**, 762 (1925); G. F. Smith and J. F. Ross, *ibid.*, **47**, 774 and 1025 (1925).

must be considered when pure substances are to be analyzed with the greatest possible accuracy, but when the weight of precipitate is small or the percentage of desired constituent low it is permissible to neglect the volume of precipitate and adsorption, especially as the errors tend to compensate one another.

SOLUBILITY OF ALKALI PERCHLORATES
(100 ml of solvent, dissolve at 25°)

Salt	Water g/100 ml	CH_3OH g/100 ml	C_2H_5OH g/100 ml	*n*-Butyl Alcohol g/100 ml	Ethyl Acetate g/100 ml
$NaClO_4$	113.9	35.9	11.13	1.50	8.43
$LiClO_4$	47.42	89.4	79.4	49.3	63.4
NH_4ClO_4	21.91	5.27	1.49	0.014	0.029
$KClO_4$	2.04	0.0830	0.0094	0.0036	0.0013
$RbClO_4$	1.33	0.0472	0.0071	0.0016	0.0014
$CsClO_4$	1.96	0.0734	0.0086	0.0048	0.001

Procedure. — If the solution to be analyzed contains sulfate, it is advisable to remove it. To about 70 ml of solution (containing not more than 0.5 g of potassium salt) add 1 ml of concentrated hydrochloric acid, heat to a gentle boil, and add hot 0.5 N barium chloride solution drop by drop until no further precipitation occurs. Wait 15 minutes; filter off the barium sulfate, and wash it with hot water.

If ammonium salts are present, evaporate to dryness in a porcelain dish and ignite carefully till all ammonium salts are decomposed. Cool, rinse down the sides of the dish with a little water, again evaporate, and ignite at a temperature below redness. Dissolve the residue in about 20 ml of water and transfer to a 150-ml Pyrex beaker.

Two methods for carrying out the perchlorate separation of potassium (rubidium and cesium) from sodium (and lithium) will be given.

The first method depends upon the use of ethyl alcohol containing a little perchloric acid to make the perchlorate of potassium practically insoluble. This is the method commonly used. H. H. Willard, however, prefers to make use of normal* butyl alcohol, and many chemists use this procedure.†

Method 1

Add 5 ml of perchloric acid, *d.* 1.12, containing 20 per cent $HClO_4$, and evaporate carefully till salts separate. Add 10 ml of hot water, 5

* Normal butyl alcohol is $CH_3·CH_2·CH_2·CH_2OH$. The word *normal* is used to distinguish it from its isomers $(CH_3)_2·CH_2·CH_2OH$ (called isobutyl alcohol) $CH_3·CH_2·CHOH·CH_3$ (called secondary butyl alcohol), and $(CH_3)_3·COH$ (called tertiary butyl alcohol). To show that the word *normal* does not refer to normal concentration, the small letter *n* will be used in the directions, whereas N will signify normal in the sense of concentration.

† Cf. Hillebrand and Lundell, *Applied Inorganic Analysis.*

ml more of perchloric acid, and again evaporate on a water-bath and finally on a sand-bath. If dense fumes of perchloric acid are not evolved, repeat the addition of water and perchloric acid until dense fumes are obtained by evaporation. Cool to below room temperature and add 20 ml of 97 per cent alcohol containing 0.2 per cent of perchloric acid and saturated with potassium perchlorate.* Crush the precipitated $KClO_4$ with the end of a stirring-rod and allow to stand for 30 minutes, preferably with the dish resting in ice water. Filter through a Gooch or Munroe crucible that has been dried at 120–130° and weighed.

If only a small precipitate is obtained, it is safe to wash and weigh it at once without purification provided no considerable quantity of other salt is present in the alcoholic solution. Unless the absence of much sodium or other salt is assured, decant the solution through the filter and wash the crystals three times with small portions of alcohol containing 0.2 per cent of perchloric acid. Then dissolve the crystals in a little hot water, add 1 ml of perchloric acid, evaporate, and treat as before. Transfer the pure potassium perchlorate to the weighed filtering crucible and wash with small portions of cold alcohol† which is saturated with $KClO_4$ besides containing 0.2 per cent of $HClO_4$. Dry at 130° for an hour and weigh.

Method 2

In this procedure the alkali perchlorates are digested with a mixture of *n*-butyl alcohol and ethyl acetate in which the perchlorate of potassium (rubidium and cesium) is insoluble. After filtering off the potassium perchlorate, the sodium can be precipitated as sodium chloride by adding a solution of hydrogen chloride gas dissolved in butyl alcohol. Then, if lithium is present, it can be weighed as sulfate after evaporating the filtrate from the sodium chloride precipitation.

To the solution of chlorides add 2 or 3 times as much of 9 *N* perchloric acid as is theoretically necessary to convert the chlorides to perchlorates (not less than 1 ml in any case). Evaporate to dryness on the

* One hundred milliliters of the alcohol containing perchloric acid will dissolve 2.8 mg of $KClO_4$. If considerable $NaClO_4$ is present it tends to salt out a little $KClO_4$ from the saturated alcoholic solution. When considerable sodium salt is present, therefore, it is advisable to wash the first precipitate with a little alcohol containing no potassium perchlorate, dissolve the precipitate in a little water, and repeat the precipitation. The small quantity of sodium salt adhering to the partially washed $KClO_4$ precipitate will do no harm the second time. (Cf. Davis, *J. Agr. Sci.*, **5**, 52, 512; Gooch and Blake, *Am. J. Sci.*, **44**, 381; Baxter and Kobayashi, *J. Am. Chem. Soc.*, **42**, 735.

† Baxter and Kobayashi have shown that it is advisable to cool the wash alcohol to 0° and to keep the volume of the washings as small as possible.

hot plate, at a temperature not exceeding 350°, and expel any acid condensed on the side walls of the beaker by playing a free flame against the outside. Cool, wash down the sides of the beaker with 3 to 5 ml of hot water, and again evaporate to dryness on the hot plate. Cool; add 10 to 20 ml of a mixture of equal parts by volume of *n*-butyl alcohol and ethyl acetate. Digest near the boiling point* for 2 or 3 minutes and then cool to room temperature.

Decant the liquid through a previously ignited and weighed Gooch or Monroe crucible and wash the precipitate 3 times by decantation with 5-ml portions of the alcohol-acetate mixture. Reserve the filtrate and washings if it is desired to make a direct determination of sodium.

Dissolve the residue in the crucible with a very little hot water, catching the solution in the original beaker. Again evaporate to dryness. Add 10 ml of the butyl alcohol-acetate mixture; digest and cool as before. Filter through the original crucible, which has been dried meanwhile. Transfer the precipitate to the crucible and wash 10 to 15 times with less than 1-ml portions of the alcohol-acetate mixture. Dry the beaker and brush any particles of potassium perchlorate into the crucible. Dry an hour at 110° and 15 minutes at 350°. Cool and weigh as $KClO_4$.

To determine the sodium, evaporate the combined filtrates and washings till the volume is not over 20 ml at the most and all the ethyl acetate has been removed. Heat to 80 to 90°, and add dropwise, with stirring, 2 ml of a 20 per cent solution of hydrogen chloride in *n*-butyl alcohol (prepared by passing dry hydrogen chloride into 200 ml of butyl alcohol for 2 hours; the density of the solution is 0.905). Then add 6 ml more of the HCl-alcohol solution, cool to room temperature, filter off the precipitated sodium chloride, and wash 8 or 10 times with 1-ml portions of 6 to 7 per cent solution of hydrogen chloride in butyl alcohol. Dry 15 minutes at 110° and then for 5 minutes at 600°. Cool and weigh as NaCl or dissolve the salt in water and titrate the chloride (see Part II, III).

Remark. — The precipitation of potassium as perchlorate can be accomplished in the presence of most other cations except ammonium. The precipitate should be easily soluble in hot water. In the analysis of fertilizers it is often recommended to dissolve the precipitate in hot water, dry, and weigh again to see if any other insoluble substance was present with the precipitated potassium perchlorate.

* Be careful about using a free flame because if the combustible vapors catch fire a dangerous explosion will result.

C. Separation of Sodium from Potassium by the Uranyl-zinc Acetate Method

Principle. — By means of uranyl-zinc or uranyl-magnesium acetate solution, insoluble complex acetates containing sodium can be formed. In most cases a mixture of uranyl and magnesium acetates in dilute acetic acid is used as the reagent, although Kolthoff has shown that zinc can replace the magnesium, perhaps to advantage. In the former case, the greenish yellow precipitate corresponds to the formula $(UO_2)_3MgNa(C_2H_3O_2)_9 \cdot 6\frac{1}{2}H_2O$ when dried at a temperature not exceeding 110° and contains 1.53 per cent of sodium. It serves for the determination of sodium in quantities of 0.5 to 50 mg but is so bulky that it is unsuitable for larger quantities. The presence of more than 2 mg of lithium or 0.2 g of potassium causes interference and high results; small quantities of rubidium, cesium, ammonium, or alkaline earths do no harm. Phosphates and arsenates must be absent.

Reagent. — Dissolve, separately, 85 g of $UO_2(C_2H_3O_2)_2 \cdot 3H_2O$ and 500 g of $Mg(C_2H_3O_2)_2 \cdot 4H_2O$ in 1 l of normal acetic acid. Heat each solution to about 70°, mix at this temperature, and allow to cool to 20°. Keep at this temperature for at least an hour and filter. In this way 2 l of reagent are obtained, of which 100 ml should be used when the quantity of sodium present is 10 mg or less and in all cases 10 ml are desirable for each milligram of sodium likely to be present.

Procedure. — Concentrate the aqueous solution, preferably of chlorides, to 5 ml, or less, if there is no separation of solid salt. Add 10 ml of reagent for each milligram of probable sodium content, using not less than 100 ml in any case, place in a beaker of water at 20° and stir vigorously for 30–35 minutes. Filter into a weighed Gooch, Munroe or glass filtering crucible and wash with 5-ml portions of 95 per cent ethyl alcohol which has been saturated with solid uranyl-magnesium-sodium acetate. (If ordinary 95 per cent ethyl alcohol is used, assume that each 5 ml dissolves 1 mg of the precipitate.) Dry at 105° for 35 minutes.

Remarks. — (1) Instead of weighing the precipitate, the uranium content can be determined by titration with standard disodium hydrogen phosphate (35 g $Na_2HPO_4 \cdot 12H_2O$ per liter) using potassium ferrocyanide test paper (filter paper dipped in 10 per cent potassium ferrocyanide solution and dried) as an outside indicator. Moisten the precipitate with 2–2.5 ml of glacial acetic acid and dissolve it in 40–50 ml of hot water. Titrate at 90° with the phosphate solution until a drop of the clear solution, free from any uranyl phosphate precipitate, will not give a brown color when placed on a piece of the test paper.

(2) If more than 2 mg of lithium is present it should be removed, and this is best accomplished by precipitation as fluoride. The excess fluoride must then be removed by evaporating in platinum with hydrochloric acid. This is accomplished as follows:*

To not more than 0.1 g of the salt add 10 ml of water and 5 ml of 95 per cent alcohol. After the salt has dissolved, add 5 ml of 10 per cent ammonium fluoride solution to which a little ammonium hydroxide has been added to decompose any fluosilicate which is likely to be present in the reagent. After standing for at least 20 hours, filter off the precipitate of Li_2F_2 and wash it five times with 2-ml portions

* Cf. Barber and Kolthoff, *J. Am. Chem. Soc.*, **51**, 3233 (1929).

of 50 per cent alcohol containing 0.5 per cent of ammoniacal ammonium fluoride. Evaporate the filtrate to dryness in a platinum dish and moisten the residue with 5 ml of concentrated hydrochloric acid. Evaporate to dryness and repeat this treatment with hydrochloric acid twice more after which it can be assumed that the final, dry residue contains neither lithium nor fluoride.

(3) If more than 0.2 g of potassium is present, the greater part should be removed by treatment with perchlorate. This treatment also serves to remove rubidium and cesium which, however, cause less interference. To determine sodium in commercial potassium chloride, dissolve 1 g of the salt in 5 ml of water and add a hot solution of 2 g of NH_4ClO_4 in 3 ml of water. Cool to room temperature, filter, and wash the precipitate five times with 2-ml portions of 95 per cent alcohol. Evaporate to dryness, heat strongly, and determine sodium in the residue.

(4) The presence of phosphate or arsenate interferes with the determination of sodium as complex acetate. They should be removed by treatment with "magnesia mixture." Evaporate the filtrate to dryness, heat to expel ammonium salts, treat the residue with hot water, filter and use the filtrate for the sodium determination.

D. Separation of Potassium as Cobaltinitrite

Sodium cobaltinitrite is probably the most sensitive precipitant of potassium ions in aqueous solution. Biilmann* was able to detect 0.0009 mg of potassium in the presence of 4000 equivalents of sodium. Since de Koninck† recommended the reaction in 1881, the quantitative determination of potassium as cobaltinitrite has been studied by many chemists, some of whom have been able to get satisfactory results.

Produced under ideal conditions, the precipitate, formed in dilute acetic acid solution with a considerable excess of the reagent, corresponds to the formula, $K_2NaCo(NO_2)_6$, with 17.93 per cent of potassium, equivalent to 21.37 per cent K_2O. From saturated NaCl solutions, the precipitate has the formula $K_3Na_3[Co(NO_2)_6]_2$.

The reagent, sodium cobaltinitrite, is not very stable, and the composition of the precipitate varies somewhat when produced under different conditions. For this reason, Vürtheim and others have recommended the use of empirical factors, and the Association of Official Agricultural Chemists has abandoned the method although many of its cooperating chemists obtained excellent results.

The precipitate can be filtered, dried at 110° and weighed without decomposition, it may be dissolved and the cobalt determined electrolytically,‡ the nitrite may be determined volumetrically,§ or the volume of the precipitate may be measured in a graduated centrifuge tube.

* *Z. anal. Chem.*, **39**, 284 (1900).

† *Ibid.*, **20**, 390 (1881).

‡ Dissolve the precipitate in dilute hydrochloric acid, boil to decompose the nitrite, and carry out the electrolysis as described under Cobalt.

§ Boil the washed precipitate with dilute sodium hydroxide, filter off the cobaltic hydroxide, make the filtrate acid and titrate with permanganate as described under *Volumetric Analysis, Analysis of Nitrous Acid;* 1 ml of 0.1 N $KMnO_4$ = 0.000785 g K_2O. Another method — Wash the precipitate into a measured volume of hot permanganate solution diluted with ten times as much water. After 5–6 minutes make acid with 5 N H_2SO_4 and titrate the excess permanganate with standard oxalate solution. In this case, 1 ml 0.1 N $KMnO_4$ = 0.000856 g K_2O.

Reagent. — Dissolve 28.6 g of cobaltous nitrate crystals and 50 ml of glacial acetic acid in enough water to make 500 ml of solution. Dissolve 180 g of sodium nitrite in 500 ml of water. Keep these two solutions separate until the day before the analysis is to be made, then mix equal volumes, shake or stir well, allow to stand over night in a glass-stoppered bottle, and filter just before using.

Procedure. — The potassium solution should contain the equivalent of 0.25 g KCl, or less, in a volume of 25 ml. For this weight of potassium salt use 40 ml of the filtered reagent. For smaller quantities of potassium, use less solution and less reagent but never less than 10 ml of either. Shake the mixture vigorously for several minutes, or, better still, stir mechanically for 30 minutes and allow to stand over night. Filter through a Gooch crucible, wash with 10 per cent acetic acid until the filtrate comes through colorless and then with 95 per cent alcohol. Dry at 110° for 2 hours.

Remark. — The presence of sodium salts in considerable excess does no harm. Most other cations can be removed by adding sodium carbonate solution. Ammonium salts should be removed, when present, by evaporating to dryness and gently igniting the residue. In fertilizer analysis, a fairly large sample should be taken and an aliquot part used for the potassium determination after the removal of ammonium salts and precipitation of other cations with sodium carbonate. Clerfeyt tested the method and obtained satisfactory results with materials containing from 5 to 62 per cent of K_2O. In most cases the agreement between the cobaltinitrite method and the chloroplatinate method was nearly, if not quite, as good as is usually obtained with duplicate analyses by the chloroplatinate method. When these directions are followed, the method appears to be rapid, exact, and economical.

Determination of Potassium in a Silicate*

Most silicates are decomposed by treatment with hydrofluoric acid in the presence of a dehydrating agent such as sulfuric acid, concentrated hydrochloric acid, or perchloric acid. The perchlorates of all the common cations, except those of potassium and ammonium, are soluble in alcohol.

Procedure. — To about 0.3 g of silicate in a platinum crucible add 1.5 ml of 2 N $HClO_4$ and 3–4 ml of 48 per cent HF. Evaporate to dense fumes of $HClO_4$ heating at a low temperature on a sand-bath in a larger crucible (Fig. 14) or in a wire gauze chamber made by bending some fairly fine-meshed copper or bronze gauze and inserting a triangle to hold the crucible. Cool, add water to fill about two-thirds of the crucible, heat just to boiling, filter and wash thoroughly with hot water. Evaporate the filtrate till fumes of $HClO_4$ are again obtained. Cool and add 25 ml of 97 per cent alcohol. Break up the residue with a stirring-

* J. J. Morgan, *J. Ind. Eng. Chem.* **13**, 225 (1921); M. M. Green, *ibid.*, **15**, 163 (1923).

rod* and filter through a Gooch crucible. Wash the precipitate with 1 per cent perchloric acid in alcohol. Transfer the washed precipitate and the asbestos mat to a filter and wash thoroughly with hot water to dissolve the $KClO_4$. Some insoluble salts are usually left on the filter. To the filtrate add 1 ml more of perchloric acid, evaporate to fumes, and treat with alcohol when cold. Usually the precipitate is now pure $KClO_4$. Filter, wash with 1 per cent perchloric acid in alcohol, dry for 1 hour at 110°, and weigh as $KClO_4$.

LITHIUM, Li. At. Wt. 6.94

Forms: Li_2SO_4 and LiCl

The determination of lithium in the form of the above salts is carried out in practically the same way as that of potassium. It should be mentioned, however, that on evaporating a lithium salt with concentrated sulfuric acid the acid salt, $LiHSO_4$, is formed, which on gentle ignition (even without the addition of ammonium carbonate) is changed to difficultly volatile Li_2SO_4.

Since lithium chloride is a very hygroscopic salt, it is necessary to weigh it out of contact with moist air. To accomplish this, place the platinum crucible, after being gently ignited, together with a glass-stoppered weighing beaker in a desiccator which is provided with a calcium chloride tube. After both crucible and beaker have assumed the temperature of the room, quickly place the former within the latter and stopper. Allow the weighing beaker to stand for 20 minutes in the balance case and then weigh. Place the salt in the crucible and repeat the above process.

Determination of Lithium, Potassium, and Sodium in the Presence of One Another

After determining the weight of the combined chlorides, determine the potassium in one portion as K_2PtCl_6, $KClO_4$ or $K_2NaCo(NO_2)_6$ and in a second portion determine the lithium according to one of the following methods:

(a) *Gooch's Method*†

Principle. — Anhydrous LiCl is soluble in anhydrous amyl alcohol (10 ml of cold amyl alcohol dissolve 0.66 g LiCl) while KCl and NaCl are difficultly soluble in this liquid (10 ml dissolve 0.3 mg NaCl and 0.4 mg KCl).

* This is important. If the crystals are not fine, it will be necessary to repeat the following purification process.

† *Proc. Am. Acad. Arts Sciences,* **22** [N. S. 14], 177.

Procedure. — Place the concentrated solution, containing not more than 0.2 g LiCl, in a 50-ml Erlenmeyer flask, add 5–6 ml of amyl alcohol (boiling point 132°) and carefully heat on an asbestos plate. The aqueous solution at the bottom of the beaker soon begins to boil and the water vapor escapes through the upper layer of amyl alcohol. To prevent loss by bumping at this point, it is well to pass air through the liquid during the boiling; the water evaporates more quickly and without bumping. As soon as all the water has been boiled off, the chlorides of sodium and potassium separate out and nearly all the lithium chloride dissolves in the alcoholic solution. During the evaporation of the aqueous LiCl solution, however, some LiOH is formed by hydrolysis, and the latter compound is insoluble in amyl alcohol. To dissolve this, add 2–3 drops of concentrated hydrochloric acid, boil 2 or 3 minutes, and filter while still warm through a small asbestos filter. The insoluble residue is composed of sodium and potassium chlorides. Wash it with hot amyl alcohol, which has been boiled. Evaporate the filtrate to dryness, and dissolve the residue in a little water and a little dilute sulfuric acid. Filter off the carbonaceous residue into a weighed platinum crucible, evaporate as far as possible on the water-bath, remove the excess of sulfuric acid by gentle heating over a flame (the crucible being placed in an inclined position), and then weigh. The lithium sulfate thus obtained will contain small quantities of potassium and sodium sulfates if the corresponding cations are present. To correct for these impurities subtract 0.00041 g for every 10 ml of the filtrate (exclusive of the alcohol used in washing the residue) if only sodium chloride is present, 0.00051 if only potassium chloride is present, and 0.00092 if both sodium and potassium chlorides are present.

If only 10–20 mg of lithium chloride were present in the original salt mixture, then, after filtering and washing with amyl alcohol, dissolve the residue in a little water, repeat the above treatment, and determine the lithium in the combined filtrates.

(b) *Rammelsberg's Method (Modified by F. P. Treadwell)*

Principle. — Anhydrous lithium chloride is soluble in a mixture of equal parts alcohol and ether which has been saturated with hydrogen chloride gas, whereas the chlorides of sodium and potassium are practically insoluble.

Procedure. — Evaporate the solution of the chlorides to dryness in a small Jena flask which is provided with a ground-glass, two-way stopper (p. 48, Fig. 29*a*). During the evaporation pass a current of

dry air into the flask through the long tube *a* and out through the short tube *b*. As soon as the residue has become dry, place the flask in an oil-bath and heat for half an hour at 140–150° while passing dry hydrogen chloride gas through the flask. Allow the flask and its contents to cool with the hydrogen chloride still passing through the flask. Treat the cold residue with a few milliliters of absolute alcohol, which has been saturated with hydrogen chloride gas and afterwards diluted with an equal volume of absolute ether. Tightly stopper the flask and allow it to stand with frequent shaking for 12 hours. Pour the solution through a filter which is wet with the ether-alcohol mixture, and wash the residue three times by decantation with ether-alcohol. Add a little more ether-alcohol to the contents of the flask and again allow it to stand for 12 hours; pour off the liquid and wash the residue with ether-alcohol until a trace of the residue tested in the spectroscope shows the absence of lithium. Carefully evaporate the ether-alcohol extract to dryness on a water-bath containing lukewarm water, moisten the residue with a few drops of dilute sulfuric acid, dissolve in as little water as possible, transfer to a weighed crucible, and treat with sufficient sulfuric acid to transform the lithium chloride into sulfate. Evaporate the solution as far as possible on the water-bath, then cautiously over the free flame, gently ignite, and weigh the residue of lithium sulfate.

Remark. — In the presence of considerable sodium and potassium salts it is advisable to remove the greater part of these by precipitation with hydrochloric acid gas (cf. p. 65), filtering through asbestos and washing the precipitate with concentrated hydrochloric acid until the residue no longer gives the lithium spectrum. The results obtained by this method are satisfactory.

Example for practice: Lepidolite analysis. (See Index.)

Indirect Determination of Lithium and Sodium or Lithium and Potassium

The mixture of the two chlorides is weighed and the chlorine determined either gravimetrically or volumetrically.

Separation of Potassium, Rubidium, and Cesium

Rubidium and cesium, when either is present alone, can be determined by any of the methods described for potassium. The solubility of the chloroplatinates, cobaltinitrites, and perchlorates of potassium, rubidium, and cesium decreases in the order named. The qualitative separation described in Vol. I of this book is probably as good as any that has been devised. In this procedure, sulfate is first removed by precipitation with lead nitrate in the presence of dilute nitric acid. After filtering off the lead sulfate, the excess lead is removed by saturating the solution with hydrogen sulfide. The cesium, rubidium, and potassium are then precipitated together as perchlorates, as described on pp. 63, 64 for the determination of potassium, and

the filtrate from this precipitation will contain sodium and lithium. The perchlorates of cesium, rubidium, and potassium are dissolved in a little hot water, converted into cobaltinitrites, as described on p. 68, and filtered off. This precipitate, together with a little sodium nitrite solution, is heated until the mass fuses and effervesces no more, the residue is taken up in water and a little dilute acetic acid and the black cobalt oxide residue is rejected. The solution of alkali nitrites is treated with sodium nitrite and bismuth nitrate solution to precipitate $Cs_2NaBi(NO_2)_6$ and $Rb_2NaBi(NO_2)_6$, leaving potassium nitrite in solution. The precipitate is treated with hydrochloric acid and, in the resulting solution, cesium is precipitated as $Cs_3Sb_2Cl_9$. After filtering off this precipitate, the rubidium is precipitated as $RbHC_4H_4O_6$ and finally converted into $Rb_2NaBi(NO_2)_6$ again. The separation is imperfect because the difference in the solubility of the corresponding cesium and rubidium salts is not great enough to permit a complete separation. The procedure can be carried out and approximately correct results obtained quantitatively if more time is allowed for the complete precipitation of the cobaltinitrites and of the alkali-bismuth nitrites.

The following procedure, which is based upon one proposed by Strecker and Diaz* gives fairly satisfactory results when but little potassium is present.

Procedure. — Dissolve the chlorides,† free from ammonium salt, in a little water and slowly add, while stirring, a mixture of concentrated hydrochloric acid diluted with twice as much 95 per cent alcohol. Filter off the precipitated KCl (and NaCl if present), wash with absolute alcohol, dry at 110°, and weigh. Heat the filtrate to boiling and treat with a boiling-hot, concentrated solution of $SnCl_4$ which has been dissolved in a mixture of one part concentrated hydrochloric acid and two parts alcohol. Allow to cool, and after 4 hours filter off the precipitate of Cs_2SnCl_6 and Rb_2SnCl_6, wash with absolute alcohol, dry at 100°, and weigh. If it is desired to determine the potassium, treat the filtrate with perchloric acid and determine the potassium not removed as chloride by the treatment with hydrochloric acid and alcohol. Add the corresponding weights of both precipitates to obtain the total potassium content. Dissolve the weighed chlorostannates in 5 per cent tartaric acid solution, saturate with hydrogen sulfide, and filter off the stannic sulfide precipitate. Evaporate the filtrate to dryness, and ignite carefully to destroy the tartaric acid.

Treat the residue with an equal weight of $FeCl_3$ and dissolve in as little water as possible. Add 5 ml of glacial acetic acid for each 0.1 g of mixed chlorides and heat just to boiling. Add a cold, 30–40 per cent solution of $SbCl_3$ in glacial acetic acid, digest 1 hour on the water-bath, cool and allow to stand for at least 12 hours. Filter through a Gooch, Munroe, or glass filtering crucible, and wash the precipitate of $Cs_3Sb_2Cl_9$ with a 5–10 per cent solution of $SbCl_3$ in glacial acetic acid.

* *Z. anal. Chem.*, **67**, 321 (1925).

† Perchlorates can be converted into chlorides by careful ignition.

If considerable rubidium was present, it is necessary to dissolve this precipitate in hydrochloric acid and repeat the precipitation with $SbCl_3$. The second precipitate should be pure.

Dissolve the final precipitate of $Cs_3Sb_2Cl_9$ in hydrochloric acid, dilute until it is approximately 0.3 N in acid, disregarding any SbOCl precipitate that may form, saturate with hydrogen sulfide, filter off the Sb_2S_3, evaporate the filtrate to dryness, and determine the cesium as $CsClO_4$ as described for the determination of potassium on p. 63. Deduct the corresponding weight of Cs_2SnCl_4 from the weighed mixture obtained above to obtain the weight of

AMMONIUM, NH_4. Mol. Wt. 18.04

Forms: NH_3, NH_4Cl, $(NH_4)_2PtCl_6$, Pt, N_2

There are two cases to distinguish: (1) The ammonium is present as chloride in aqueous solution. (2) The ammonium is present in solution together with other cations and anions.

1. The Solution Contains only NH_4^+ and Cl^- Ions

In this case the solution can be evaporated to dryness and the residue of ammonium chloride weighed; or the ammonium can be precipitated as $(NH_4)_2PtCl_6$ and the precipitate weighed; or the ammonium chloroplatinate can be ignited and the residue of platinum weighed.

(*a*) Determination as NH_4Cl

Add concentrated HCl to the aqueous solution and evaporate to a small volume on the water-bath at as low a temperature as possible, transfer the solution to a crucible, evaporate on the water-bath to dryness, and heat the covered crucible to constant weight in a drying-oven. Good results are obtained, but they are always a little low. On evaporating the aqueous solution some NH_4Cl is driven off, and the amount lost increases in proportion to the quantity of water used and the temperature at which the evaporation takes place. In cold, aqueous solution, ammonium chloride is largely ionized, $NH_4Cl \rightarrow NH_4^+ + Cl^-$. As the temperature is raised, hydrolysis takes place to an appreciable extent, $NH_4Cl + H_2O \rightarrow NH_4OH + HCl$, and NH_3 evaporates from the ammonium hydroxide noticeably faster than does hydrogen chloride.

If, however, a little hydrochloric acid is added to the solution the hydrolysis is prevented and the loss of NH_3 is reduced to a minimum. The ammonium chloride must be dried in a covered crucible as otherwise a small quantity of the salt will be lost, but this loss is small in comparison with the possible loss during the evaporation.

(*b*) Determination as $(NH_4)_2PtCl_6$

On heating $(NH_4)_2PtCl_6$ to 130° the salt is unchanged. An aqueous solution containing HCl, NH_4Cl and an excess of H_2PtCl_6 can be evaporated to dryness without appreciable loss of NH_3. To the aqueous solution of ammonium chloride, therefore, add an excess of chloroplatinic acid and a little hydrochloric acid. Evaporate to dryness at as low a temperature as possible. Pour absolute alcohol over the residue to dissolve the excess of H_2PtCl_6, break up the crystals with a stirring-rod, and filter through a Gooch crucible. Dry at 130° and weigh.

(*c*) Determination as Platinum

Instead of weighing the $(NH_4)_2PtCl_6$ as such, it can be decomposed by ignition and the weight of the residual platinum determined. As ammonium chloroplatinate decrepitates strongly on being heated, the ignition must take place in a large porcelain crucible, which is provided with a close-fitting cover. The precipitate must be heated gradually at first to prevent loss. It is best ignited according to the directions of Rose. Place the precipitate and filter in the crucible with the filter paper on top, cover the crucible, and heat over a small flame until the paper is completely charred without allowing the vapor to escape visibly from the crucible. Then heat the crucible with a hotter flame, allowing free access of air into the inclined crucible, until the charred filter is completely consumed.

2. The Ammonium is Present Together with Other Cations and Anions in Solution or in Solid Form

The solution is distilled after the addition of a strong base (NaOH or $Ca(OH)_2$), the ammonia evolved is absorbed in hydrochloric acid, and the resulting solution is analyzed according to 1.

Procedure. — Place about 0.5 g of the substance to be analyzed in the 400–500 ml Erlenmeyer flask *K*, Fig. 31, dissolve it in 200 ml of water, add a few drops of litmus or phenolphthalein indicator* solution, and if the solution reacts acid, slowly add through *T* some 12 *N* sodium hydroxide solution (which has been previously boiled to expel traces of ammonia) until the color of the solution (well-mixed by shaking) shows a basic reaction; then add 5 ml more of the caustic soda solu-

* An excess of strong caustic alkali solution will decolorize phenolphthalein. Only a little more than enough NaOH to turn the phenolphthalein pink is necessary.

tion.* Heat the liquid to boiling and carefully distil 100 ml into the receiver *V*, containing 30 ml of 0.5 *N* hydrochloric or sulfuric acid. To make sure that no ammonia escapes from the receiver it is well

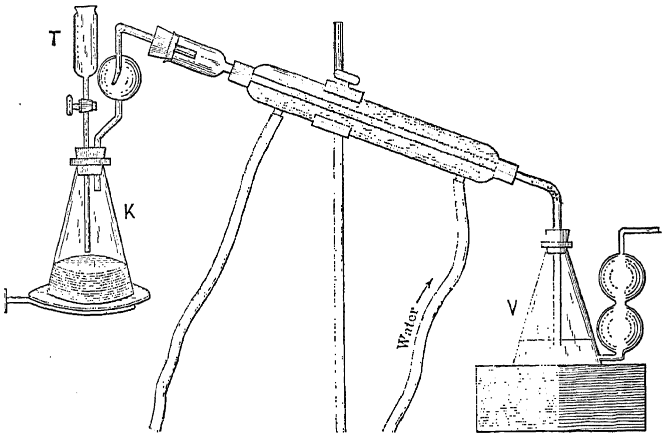


FIG. 31.

to connect it with a second absorption flask containing 5 ml of 0.5 *N* acid and some distilled water.

After 100 ml of the liquid has distilled over, all the ammonia will be found in the receiver and can be determined according to 1 (*a*) or 1 (*b*); preferably the latter. The determination can be carried out much more quickly, however, if the receiver contains a measured amount of standardized acid and the excess is determined after the distillation by titration with methyl orange or methyl red as indicator (cf. Alkalimetry).

It is also possible to make an accurate determination of the amount of ammonia present by measuring the volume of the gas.†

Colorimetric Determination of Ammonium

For the determination of such small quantities of ammonia as occur in drinking-water, the above methods are not suited. In this case the procedure is the same as was described in Vol. I, under *Ammonium*. (For mineral waters it is necessary to add more than one drop of the soda solution, the amount necessary being determined by adding litmus to a definite volume of the water and then adding the soda

* The separatory funnel *T* should be roughly calibrated before setting up the apparatus, by pouring water into it, 1 ml at a time, and marking with a pencil the level of the liquid on the glass.

† Cf. Part III, Gas Analysis.

solution until the litmus changes to blue.) Receive the distillate in 50-ml graduated Nessler tubes (in the fourth one there is usually no ammonia to be detected) and Nesslerize these. To do this, mix 50 ml of distillate with 2 ml of Nessler solution and compare the color produced with the colors obtained similarly from a series of tubes containing known amounts of ammonia. When a standard is found of the same shade as the solution tested, then the two solutions contain the same amount of ammonia.

Prepare the ammonium chloride standards as follows: Dissolve 3.141 g of ammonium chloride, which has been dried at 100°, in 1 l of water free from ammonia (cf. Vol. I, under *Ammonium*). The solution now contains 1 mg of ammonia (NH_3) per milliliter; this, however, is too strong for most purposes. Take 10 ml and dilute to 1 l. Of this solution 1 ml contains 0.01 mg NH_3. If the water to be analyzed contains considerable ammonia, a smaller portion should be taken for the analysis than in ordinary cases (500 ml), as otherwise the first distillate (50 ml) would give too intense a color with the Nessler solution. In such a case use only 50 ml of the water for the analysis and dilute to 500 ml with water free from ammonia and then distilled.

To determine how much should be taken for the analysis, make the following experiment:

Place about 100 ml of the water to be tested in a narrow cylinder (which is provided with a ground-glass stopper), add 2 ml of a strongly alkaline sodium carbonate solution* to precipitate the calcium which may be present, shake the mixture vigorously, and allow the precipitate to settle. From the clear supernatant liquid pipet off 50 ml into a Nessler tube, treat with 2 ml of Nessler solution and mix.† If a strong yellow color, or even a precipitate, is obtained, then take only 50 ml of the water for analysis. If, on the other hand, not more than a faint coloration is apparent, use 500 ml for the determination.

For the Nesslerization, place the three cylinders each containing 50 ml of the distillate over a sheet of white paper, add 2 ml of the Nessler reagent, and mix. Beside them place a series of similar cylinders containing respectively 0.0, 0.5, 1.0, 1.5, 2.0, 2.5, 3.0 ml of the standard ammonium chloride solution diluted to 50 ml. Treat these also with

---

* Fifty grams NaOH and 50 g Na_2CO_3 (calcined) dissolved in 600 ml of pure distilled water and the solution boiled until the volume is only 500 ml.

† In mineral waters rich in magnesium sulfate, the addition of the 10 ml of sodium carbonate solution often fails to prevent a turbidity on adding the Nessler reagent, which would render a colorimetric determination impossible. In this case add 10 ml of a boiled $BaCl_2$ solution (120 g $BaCl_2 \cdot 2H_2O$ in 500 ml H_2O) before treating the water with the sodium carbonate solution.

2 ml of the Nessler reagent and match the colors obtained in the test with those obtained from known amounts of ammonia.

The Nessler reagent should give a distinct coloration with 500 ml of water containing 0.005 mg NH_3; if it does not, it must be made more sensitive by the addition of mercuric chloride solution.

For mixing the liquid in the cylinders it is convenient to employ a stirrer such as is shown in Fig. 32, the diameter of the bulb on the end being only slightly less than that of the cylinder. By moving this stirrer up and down twice, the liquid becomes thoroughly mixed.

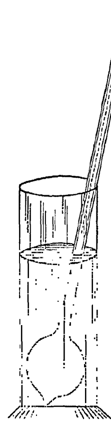


FIG. 32.

Kjeldahl's Method for Determining Nitrogen

The methods which have been described thus far are suitable only for the determination of nitrogen when it is in solution in the form of NH_4^+ ions. It is, however, of great importance to be able to determine nitrogen when it is present other than as an ammonium compound (in protein, coal, etc.). The Kjeldahl method converts such nitrogen into ammonium salt.

By heating nitrogenous organic substances with concentrated sulfuric acid, potassium permanganate, mercuric oxide, etc., the organic matter is destroyed and the nitrogen is completely changed to ammonium and held as ammonium acid sulfate, from which the ammonia can be readily distilled. Selenium is an excellent catalyst for this reaction. Cf. p. 78.

Procedure. — Place from 0.7 to 3.5 g of substance, according to the nitrogen content, in a 500–600 ml Kjeldahl digestion flask. This is made of difficultly fusible potash glass and has a long neck to act as a condenser during the digestion process. Add about 0.7 g of mercuric oxide or 0.65 g of mercury, and 2–30 ml of concentrated sulfuric acid. Place the flask in an inclined position and heat very gently until the substance is thoroughly wet with the acid and frothing ceases. Then gradually raise the temperature until the acid boils and is nearly, if not quite, colorless. Usually 90 minutes' digestion is sufficient.

Allow to cool, dilute to about 200 ml, add a few pieces of zinc or pumice to prevent bumping, and 25 ml of potassium sulfide solution (40 g to the liter). This causes the precipitation of black mercuric sulfide. Add sufficient strong sodium hydroxide solution to make the solution alkaline (80 ml of 12 N NaOH should be sufficient), pouring it down the side of the flask so that it does not mix with the acid. Quickly connect with a condenser and distil off the ammonia into a measured volume of standard acid as in the analysis of an ammonium salt.

Figure 33* shows how a series of analyses can be carried out simul-

* From Scott's *Standard Methods of Chemical Analysis.*

taneously in a busy laboratory. The Hopkins' distillation tubes used to connect the distilling flasks with the condensers are useful in preventing errors by bumping.

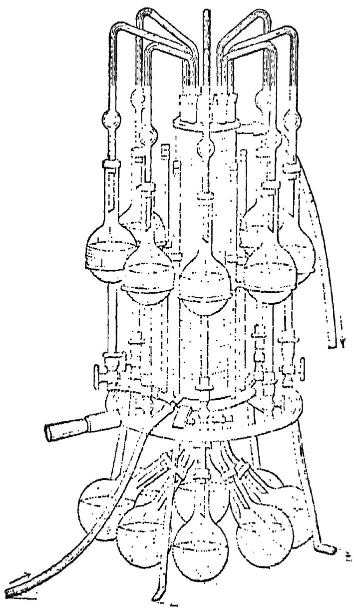


FIG. 33.

Always make a blank test with all the reagents using about 1 g of sugar for the digestion. The sugar serves to reduce any nitrates that are present in the reagents.

Gunning's Method for Determining Nitrogen

Instead of using mercuric oxide or mercury as a catalyzer in the digestion of organic materials, Gunning has recommended the use of 10 g of pure potassium sulfate. Usually the digestion is accomplished just as quickly and it is unnecessary to add potassium sulfide. The solution is, therefore, clear during the distillation and there is less danger of bumping. The procedure is the same otherwise. The time required for the digestion is greatly shortened if 25 ml of a 2 per cent solution of H_2SeO_3 is concentrated sulfuric acid is added together with the K_2SO_4.

The Kjeldahl and Gunning methods will usually give the nitrogen present as nitrate if the original digestion is made with 30 ml of concentrated sulfuric acid containing 1 g of salicylic acid. Allow the acid mixture to stand 30 minutes with frequent shaking, add 5 g of $Na_2S_2O_3$, and heat 5 minutes. Then add 10 g of K_2SO_4 (or Na_2SO_4) and digest in the usual way.

Osborn and Krassitz* have shown that a mixture of mercuric oxide and selenium is a very efficient catalyst. Taylor† found in determining the nitrogen content of cereal products that, after 30 minutes' digestion of 1 g of sample with the usual quantity of concentrated sulfuric acid and 10 g of a mixture of 100 parts $Na_2SO_4 \cdot 7H_2O$, 7 parts HgO, and 1.5 parts Se, better values were obtained than after 90 minutes' digestion with acid and HgO alone.

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* *J. Assoc. Official Agr. Chemists*, **16**, 110, 113 (1932).

† *Ind. Eng. Chem.*, **5**, 263 (1933).

MAGNESIUM, Mg. At. Wt. 24.32

Forms: $MgSO_4$, $Mg_2P_2O_7$, $MgNH_4PO_4 \cdot 6H_2O$, $Mg(C_9H_6NO)_2$

(a) Determination as $MgSO_4$

This method for the determination of magnesium can always be employed when the magnesium is combined with an acid which can be volatilized by heating with sulfuric acid, and when no basic constituent other than ammonium is present.

Place 0.5 g of the substance in a crucible and add about 2 ml of concentrated sulfuric acid. Substances which react violently with concentrated H_2SO_4 should be first treated with water, and dilute sulfuric acid added little by little. Evaporate on the water-bath as far as possible, and remove the excess of sulfuric acid by cautiously heating the crucible, held in an inclined position, over a free flame. Finally, heat the dry mass just to redness in a covered crucible, cool in a desiccator, and weigh as quickly as possible, as the anhydrous magnesium sulfate is hygroscopic.

(b) Determination as Magnesium Pyrophosphate

This, the most important of all the methods for the determination of magnesium, is always applicable and depends upon the following principles: If the solution of a magnesium salt is treated with an alkali orthophosphate solution in the presence of ammonium chloride and ammonia, the magnesium is completely precipitated as magnesium ammonium phosphate, $MgNH_4PO_4 \cdot 6H_2O$, which by ignition is changed to magnesium pyrophosphate:

$$2MgNH_4PO_4 \cdot 6H_2O = 2\,NH_3 + 13\,H_2O + Mg_2P_2O_7$$

Formerly it was a common practice to precipitate magnesium ammonium phosphate in the cold. Neubauer* showed, however, that this sometimes leads to high results and sometimes to low ones. The results are low when the precipitation takes place in strongly ammoniacal solutions containing but little ammonium salts, particularly when the phosphate solution is added slowly. Tribasic magnesium phosphate, $Mg_3(PO_4)_2$, contaminates the precipitate. On the other hand, the results are too high if the precipitation takes place in neutral or slightly ammoniacal solution in the presence of considerable ammonium salts. In this case more or less monomagnesium ammonium phosphate, $Mg(NH_4)_4(PO_4)_2$, is formed. This compound is changed to magnesium metaphosphate by gentle ignition:

$$2\,Mg(NH_4)_4(PO_4)_2 = 2\,Mg(PO_3)_2 + 8\,NH_3 + 4\,H_2O$$

* *Z. angew. Chem.*, **1896**, 439. See also Gooch and Austin, *Z. anorg. Chem.*, **20**, 121.

and the results are too high. When only a little of the metaphosphate is present, the temperature of the blast lamp will eventually lead to volatilization of some phosphorus pentoxide:

$$2\ Mg(PO_3)_2 = Mg_2P_2O_7 + P_2O_5$$

so that nearly correct results are then obtained.

Recent studies have shown that during the ignition of $MgNH_4PO_4$ there is likely to be a loss of phosphorus due to the reduction by hot carbon. Two ways of overcoming this difficulty have been suggested. McNabb* recommends dissolving the precipitate off the filter by means of nitric acid, making the solution slightly ammoniacal and evaporating in a weighed porcelain crucible. McCandless and Burton† recommend washing the precipitate at the last with a concentrated solution of ammonium nitrate in $1.5\,N$ ammonium hydroxide. In either case careful ignition gives a white precipitate of magnesium pyrophosphate and there is no reduction or loss of phosphorus. Schmitz‡ has shown that precipitation in the presence of ammonium acetate is advantageous.

Method of B. Schmitz§

If the original volume is over 300 ml it is well to concentrate the *acid* solution by evaporation on the hot plate. If the solution is accidentally evaporated to dryness, moisten the residue with 5 ml of $6\,N$ hydrochloric acid and enough water to dissolve ammonium salts, which are always present when the magnesium is determined in the filtrate from the precipitation of calcium oxalate. If a clear solution is not obtained, heat to boiling and filter if necessary. Wash the precipitate (usually a little silica from the glass) once with $2\,N$ hydrochloric acid and then with hot water till free from chloride.

To the acid solution add 5 g of ammonium acetate, an excess of ammonium phosphate, and a few drops of phenolphthalein solution. Heat the solution to near the boiling point and then slowly add $1.5\,N$ ammonia water until a faint pink color is obtained and a slight precipitation takes place. Stir well for about a minute, touching the sides of the beaker as little as possible. When the precipitate has become distinctly crystalline, add more ammonia until a deep color is obtained with the phenolphthalein. Allow the solution to cool, then add one-

* *J. Am. Chem. Soc.*, **49**, 891, 1451 (1927).

† *Ind. Eng. Chem.*, **16**, 1267 (1924).

‡ *Z. anal. Chem.*, **65**, 46–53 (1924); cf. McNabb, *J. Am. Chem. Soc.*, **50**, 300 (1928).

§ *Z. anal. Chem.*, **65**, 46 (1924).

fifth the solution's volume of concentrated ammonium hydroxide and allow to stand at least 4 hours, preferably over night.

Filter into a weighed Gooch crucible. Wash the precipitate with 1.5 N ammonia until free from chloride, and finally moisten it with 4–5 drops of a saturated solution of ammonium nitrate in 1.5 N ammonia. Ignite very slowly, gradually increasing the heat until the precipitate is white. After cooling, weigh the $Mg_2P_2O_7$:

$$2\ MgNH_4PO_4 = 2\ NH_3 + H_2O + Mg_2P_2O_7$$

From the weight of the latter, p, the content of magnesium or of magnesium oxide, can be calculated.

The precipitate can be filtered upon an ashless filter paper, but in all cases the ignition must be gradual, in order to obtain perfectly white pyrophosphate. By rapid ignition, some of the phosphorus is reduced by the ammonia. This reduction is likely to injure a platinum crucible. Often a black precipitate can be whitened by moistening with strong nitric acid and carefully heating. This treatment, however, should be avoided by carefully igniting the precipitate.

The precipitate has the formula $MgNH_4PO_4 \cdot 6H_2O$ when formed in cold, aqueous solutions. It can be weighed in this form, and since it will then weigh about 2.2 times as much as the corresponding weight of $Mg_2P_2O_7$, a slight error in the final weight, such as is likely to occur in igniting the precipitate, has less effect upon the final result. Above 60°, the stable form is $MgNH_4PO_4 \cdot H_2O$, and it can be weighed as such after drying for an hour at 100° with fairly satisfactory results.

To weigh the precipitate with its six molecules of water, proceed as above but omit the treatment with ammonium nitrate solution. For filtering use a Gooch crucible which has been washed with alcohol and ether, as described below, and weighed.

After removing all soluble salts by washing with 1.5 N ammonia, wash the precipitate with four 5-ml portions of ethyl alcohol, draining well after each washing. This serves to remove nearly all the adhering water. Then wash the precipitate with four 5-ml portions of ether, draining after each washing and drawing air through the crucible for 5 minutes after the last washing. Then wipe off the outside of the cold crucible, allow it to stand in a desiccator for 20 minutes, and weigh. Students find this method of handling the precipitate the easiest and quickest. The results are good. To make sure that all soluble salts have been removed, wash the weighed precipitate with some 1.5 N ammonia, and then with alcohol and ether as before. The new weight should agree with that first obtained.

Method of Epperson*

To the neutral or slightly acid solution of magnesium chloride, containing not more than 0.1 g of MgO and having a volume of about 150 ml, add 5 ml of concentrated hydrochloric acid and some methyl red

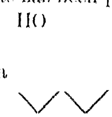
* Alice Whitson Epperson, *J. Am. Chem. Soc.*, **50**, 324 (1928).

indicator solution. Add 10 ml of 20 per cent $(NH_4)_2HPO_4$ solution and, while constantly stirring, concentrated ammonium hydroxide until the solution contains 5 ml more of this reagent than enough to make the solution neutral. Allow the solution to stand at least 4 hours or preferably over night. Filter and wash with 1.5 *N* ammonium hydroxide. Dissolve the precipitate on the filter by washing it alternately with small portions of hot 1.5 *N* hydrochloric acid and hot water. Add 1 ml of the ammonium phosphate solution and repeat the precipitation of magnesium ammonium phosphate as before in a volume of 100–150 ml. Allow the precipitate to stand at least 4 hours, filter, and wash with 1.5 *N* ammonium hydroxide until free from chloride, and then moisten with 4–5 drops of a saturated solution of ammonium nitrate in 1.5 *N* ammonium hydroxide. Ignite carefully, taking care not to let the filter paper take fire, at approximately 500° until the precipitate of $Mg_2P_2O_7$ is white, and finally at 1000° to constant weight.

By this double precipitation a normal precipitate is obtained. The precipitate can be weighed as $MgNH_4PO_4 \cdot H_2O$ or as $MgNH_4PO_4 \cdot 6H_2O$ as described above.

(*c*) Determination of Magnesium with 8-Hydroxyquinoline

8-Hydroxyquinoline, for which the trivial name *oxine* has been proposed, has the empirical formula HC_9H_6NO and the structural formula



The hydrogen of the OH group is replaceable by metal, and precipitates are produced under certain conditions when the reagent is added to solutions containing ions of magnesium, aluminum, copper, bismuth, cadmium, zinc, mercuric mercury, lead, antimony, tin, vanadium, uranium, iron, titanium, zirconium, tantalum, columbium, manganese, nickel or cobalt. The reagent, therefore, is not specific for any particular ion, but the solubility of the various precipitates varies enough so that it can be used for numerous separations. None of the precipitates is formed from strongly acid solutions. Some of them are formed from solutions containing acetic acid and alkali acetate, some from solutions which are ammoniacal, and still others from solutions which are made alkaline with sodium hydroxide. Magnesium hydroxyquinolinate is much less soluble than the corresponding calcium compound, and pure precipitates of the magnesium compound can be obtained in the presence of small quantities of calcium. The greenish yellow precipitate is crystalline, easy to handle, and forms somewhat more readily than does magnesium ammonium phosphate, but, as with that compound, large quantities of ammonium salt, especially ammonium oxalate, prevent its formation. The precipitate can be weighed as $Mg(C_9H_6ON)_2 \cdot 2H_2O$ after drying at 105° or without the water of crystallization after drying at 140°. Instead of weighing the precipitate, it can be dissolved in dilute hydrochloric acid and titrated with $KBrO_3$-KBr solution, in which case each atom of magnesium

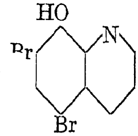
is equivalent to 8 atoms of bromine, as the following equations show:

$$Mg(C_9H_6ON)_2{\cdot}2H_2O + 2HCl = MgCl_2 + 2\,C_9H_7ON + 2\,H_2O$$
$$C_9H_7ON + 2\,Br_2 = C_9H_3ONBr_2 + 2\,HBr$$

The Br is formed when the mixture of $KBrO_3$ and KBr comes in contact with acid:

$$BrO_3^- + 5\,Br^- + 6\,H^+ = 3\,Br_2 + 3\,H_2O$$

The end point of the titration can be determined with indigo carmine as indicator, or, as is better, an excess of the $KBrO_3$-KBr solution can be added, whereby an excess of Br_2 is provided which will react with KI and liberate iodine which can be titrated with (see Iodometry). The formula of the bromine compound is



The following directions for determining magnesium as the hydroxyquinolinate will apply to a solution from which calcium has been removed as oxalate, as in the analysis of minerals.*

Reagent. — Dissolve 25 g of 8-hydroxyquinoline in 60 ml of glacial acetic acid. Dilute the solution with cold water to 2 l. One milliliter of this solution is equivalent to 0.0017 g of MgO.

Procedure. — To the solution of magnesium salt containing sufficient NH_4Cl to prevent precipitation of $Mg(OH)_2$ on adding ammonia, add NH_4OH until the solution is distinctly ammoniacal. Heat to 60–70°, and to the hot solution add, while stirring, an excess of the reagent. The excess is shown by the solutions becoming yellow. Add 4 ml of concentrated NH_4OH, stir for 10 minutes with a mechanical stirrer, and allow to stand until the precipitate has settled. Filter through a weighed Gooch crucible, wash the precipitate with hot, 0.4 *N* NH_4OH, dry at 105°, and weigh as $Mg(C_9H_6NO)_2{\cdot}2H_2O$ containing 6.988 per cent Mg or 11.56 per cent MgO.

The use of a mechanical stirrer is helpful but not absolutely necessary.

Separation of Magnesium from the Alkalies

The methods of Schmitz and of Epperson serve to separate magnesium from the alkalies if the determination of magnesium alone is desired. If it is desired to determine magnesium and the alkalies in one and the same sample, it is best to proceed as follows:†

* Redmund and Bright, *Bur. Standards J. Research,* **6,** 113 (1931).

† Gooch and Eddy, *Z. anorg. Chem.*, **58,** 427 (1908).

Schaffgottsch Method for Precipitating Magnesium*

The method is based upon the fact that magnesium can be precipitated quantitatively, by means of an alcoholic solution of ammonium carbonate, as crystalline magnesium ammonium carbonate, $MgCO_3 \cdot (NH_4)_2CO_3 \cdot 6H_2O$.

Preparation of the Precipitant. — Saturate a mixture of 180 ml concentrated ammonia, 800 ml water, and 900 ml absolute alcohol with commercial ammonium carbonate. Shake the mixture occasionally and after several hours filter off the excess of carbonate.

Procedure. — Treat the neutral solution containing only magnesium and the alkalies (lithium must not be present), preferably in the form of chlorides, with an equal volume of absolute alcohol and then with an excess of the ammonium carbonate reagent. Stir vigorously for a few minutes and allow to stand for at least half an hour. Filter through a Gooch or Munroe crucible. Wash with the precipitant, dry, ignite, and weigh as MgO.

If considerable alkali is present the precipitate always contains a small quantity of it. In such cases dissolve the precipitate in hydrochloric acid, evaporate the solution to dryness, take up the residue in a little water, and repeat the precipitation.

Evaporate the combined filtrates to dryness and determine the alkali as described on pp. 59–73.

Barium Hydroxide Method

If it is desired to separate magnesium from the alkalies in order that the alkalies may be determined, the magnesium may be precipitated as magnesium hydroxide, from a solution free from ammonium salts, by the addition of barium hydroxide solution. The barium is then removed by ammonium carbonate and the alkalies determined in the filtrate. For the detailed description of this method see Silicate Analysis. Even in this case, however, the use of the Schaffgottsch method of separating magnesium from the alkalies is more satisfactory.

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* Pogg. Ann., **104**, 482 (1858).

METALS OF GROUP IV

CALCIUM, STRONTIUM, BARIUM

CALCIUM, Ca. At. Wt. 40.08

Forms: CaO, $CaC_2O_4 \cdot H_2O$, $CaCO_3$, $CaSO_4$

1. Determination as Calcium Oxide (Lime), CaO

For the determination of calcium as CaO, it is best precipitated as the oxalate and converted to the oxide by strong ignition. The solution should contain no other cation besides magnesium and alkalies. Enough ammonium salt should be present to prevent the precipitation of $Mg(OH)_2$ upon adding ammonium hydroxide.

Procedure. — Heat the dilute, slightly acid solution to boiling and add a slight excess of hot ammonium oxalate solution. Slowly neutralize with ammonium hydroxide, while stirring, and allow the precipitate to settle for about 4 hours. Add a little more ammonium oxalate to make sure that the precipitation is complete. Decant off the clear liquid through a filter, cover the precipitate with boiling water containing ammonium oxalate,* allow to settle, filter, and repeat this washing by decantation three times. Finally transfer the precipitate to the filter and wash with a hot, very dilute solution of ammonium oxalate, until free from chloride. Place the moist filter in a platinum crucible and ignite carefully. Heat the precipitate cautiously at first, so that the too rapid evolution of carbonic oxide will not cause loss. After the filter is burnt and the precipitate is perfectly white, cover the crucible and heat strongly over a Méker burner or blast lamp for 20 minutes.

Allow the crucible to cool to about 100° in the air and then for 15 minutes in a desiccator. Weigh as CaO. Heat for another 10 minutes over the Méker burner to make sure that all the calcium carbonate has been decomposed and again weigh.

During the ignition, the following reactions take place:

$$(1)\quad CaC_2O_4 \rightarrow CaCO_3 + CO \text{ (at dull redness)}$$

$$(2)\quad CaCO_3 \rightarrow CaO + CO_2 \text{ (at about 1000°)}$$

Remarks. — With an ordinary Bunsen burner and an open crucible but little calcium oxide is formed. It is difficult to convert the precipitate completely to oxide if a *porcelain* crucible is used but if loss of heat by radiation is partly stopped by covering the *platinum* crucible, it is possible to convert 0.5 g of calcium carbonate to oxide by heating 1 hour over a Tirrill burner.

* T. W. Richards found that the calcium oxalate precipitate is appreciably soluble in pure water but practically insoluble in a dilute solution of ammonium oxalate. (*Z. anorg. Chem.*, **28**, 85 (1901)).

Most beginners make the mistake of heating precipitates too fast at the start. It is always easiest to get white products if the paper is smoked off and burned at as low a temperature as possible. To hasten the decomposition of the carbonate, the crucible may be heated within a much larger clay or graphite crucible. Saw off the bottom of the graphite crucible and make holes in the sides to hold nichrome wires, to support the crucible. Heating in such a mantle prevents some of the loss of heat by radiation, and a temperature is obtained nearly as high as that in a crucible over a blast lamp.

Calcium oxide is hygroscopic but when strongly ignited there is no difficulty in weighing it provided the above directions are followed. It is, however, never safe to assume that the first weight is correct. If the cold crucible and its contents apparently gain weight rapidly while on the balance pan, it is probable that a little calcium chloride is present, owing to incomplete washing of the precipitate. This can be removed by moistening several times with ammonium carbonate and heating after each addition of carbonate.

Sometimes a little calcium sulfate is formed by allowing the gas flame to enter the crucible. This is not a serious source of error with the illuminating gas of most American cities.

If both solutions are not boiling hot during the precipitation, the calcium oxalate forms very fine crystals; it then settles very slowly and passes readily through the filter.

Calcium oxalate is inappreciably soluble in water and dilute acetic acid containing dissolved ammonium oxalate, but readily soluble in mineral acids. One liter of pure water dissolves 10 mg of calcium oxalate.

The precipitate, when formed in a boiling solution, corresponds to the formula $CaC_2O_4 \cdot H_2O$. It can be weighed in this form after drying at 100°–105°.

2. Determination of Calcium as Sulfate, $CaSO_4$

This method is chiefly used in the analysis of calcium salts of organic acids or for the conversion of calcium oxalate to sulfate in a porcelain crucible. For this purpose heat the calcium salt in a weighed crucible until the organic matter is destroyed. Then cover the crucible with a watch glass, add some dilute sulfuric acid, and heat upon the water-bath until there is no longer any evolution of carbon dioxide. Wash off the under side of the watch glass and evaporate the liquid as far as possible on the bath. Then carefully expel excess of sulfuric acid by inclining the crucible and heating over the free flame (or in an air-bath) (cf. Fig. 14, p. 37). Ignite gently and weigh. By strong ignition calcium sulfate loses SO_3.*

Calcium may also be precipitated as calcium sulfate. Treat the neutral solution containing about 0.1 g of calcium in 25 ml with 2 ml of 6 N sulfuric acid, add four volumes of alcohol, and allow the mixture

* After heating for 1 hour to dull redness, 0.2052 g $CaSO_4$ remained unchanged in weight, but on heating with the full flame of a Teclu burner, it lost 0.0004 g in weight. On heating for 1 hour over the blast lamp it lost 0.0051 g. (J. Weber.)

to stand 12 hours. Filter, wash with 70 per cent alcohol, gently ignite in a crucible, and weigh.

3. Determination of Calcium as Carbonate, $CaCO_3$

Only in rare cases is calcium precipitated as carbonate by ammonium carbonate in the presence of ammonia. Gently ignite the filtered and washed precipitate and weigh as carbonate. After weighing, moisten the residue with a little ammonium carbonate solution, evaporate to dryness on the water-bath, and again ignite gently. This is done in order to change small amounts of calcium oxide, which may have been formed during the burning of the filter paper, back to carbonate.

In the presence of considerable ammonium chloride the precipitation of calcium by means of ammonium carbonate is never complete whereas the precipitation with ammonium oxalate always is.

If a calcium oxalate precipitate is ignited to constant weight in a porcelain crucible at a temperature ranging from 675°–800°, while a current of dry carbon dioxide is constantly being led into the crucible, the precipitate is converted into calcium carbonate.* To obtain a suitable temperature range, heat the precipitate in a 30-ml Gooch crucible, covered with a Rose crucible cover and resting in a 15-ml porcelain crucible which is heated with the full heat of a Bunsen burner. Under these conditions potassium iodide (m.p. 685°) should melt in the Gooch crucible and potassium chloride (m.p. 790°) should not. Heat the crucible slowly at first to dry the precipitate and then with the full heat of the burner for 15 minutes, continuing the current of carbon dioxide until the crucible is nearly cold.

STRONTIUM, Sr. At. Wt. 87.63

Forms: $SrSO_4$, $SrCO_3$, SrO

The determination as the sulfate is the most accurate.

Determination of Strontium as Sulfate, $SrSO_4$

Procedure. — To 100 ml of the neutral solution containing not more than 0.5 g of strontium add 5 ml of $6N$ sulfuric acid and as much alcohol as there is volume of solution. Stir well, allow the mixture to stand 12 hours, filter and wash, at first with 50 per cent alcohol to which a little sulfuric acid has been added, and finally with pure alcohol until the wash water no longer gives the sulfuric acid reaction. Dry, ignite, cool, and weigh.

* H. W. Foote and W. M. Bradley, *J. Am. Chem. Soc.*, **48**, 676 (1926).

Remarks. — Only about 0.014 g of $SrSO_4$ dissolves in 100 ml of pure water. The addition of a little sulfuric acid decreases the solubility, but if too much acid is added, the precipitate dissolves appreciably.

It is very soluble in concentrated sulfuric acid and appreciably soluble in dilute hydrochloric and nitric acids, acetic acid, and in concentrated solutions of magnesium or alkali chloride.

If considerable acid is present it should be removed by evaporation.

Determination of Strontium as Oxide, SrO, or as Carbonate, $SrCO_3$

Precipitate the strontium as carbonate, or as oxalate, and change by ignition to the oxide as described under Calcium.

Strontium carbonate is decomposed by heat more difficultly than calcium carbonate, and the determination as carbonate is very satisfactory. It is advisable to treat the precipitate as described under Calcium, although it is usually unnecessary to heat with additional ammonium carbonate.

Solubility of Strontium Carbonate in Water according to Fresenius

At ordinary temperatures, 18,045 parts of water dissolve 1 part of $SrCO_3$. In water containing ammonium carbonate the salt is much less soluble; on the other hand, ammonium chloride and ammonium nitrate increase its solubility. If calcium, strontium, magnesium, and alkali salts are present together, as in minerals and in mineral waters, the calcium and strontium are both precipitated as oxalates and transformed by ignition into the oxides or carbonates. Cf. pp. 85, 87.

Solubility of Strontium Oxalate in Water

At ordinary temperatures, 12,000 parts of water dissolve 1 part of $SrC_2O_4 + 2\frac{1}{2} H_2O$. The solubility is very much less in water containing ammonium oxalate.

Barium, Ba. At. Wt. 137.36

Forms: $BaSO_4$, $BaCrO_4$

1. Determination as Barium Sulfate

Dilute the solution so that it contains not more than 0.15 g of barium per 100 ml. Make slightly acid with hydrochloric acid, heat to boiling, and add a slight excess of hot, normal sulfuric acid. Use about 3 ml of normal acid for each 100 ml of solution. After the precipitate has settled, add a little more sulfuric acid to make sure that the precipitation is complete. After standing an hour or more in a warm place, decant the solution through a filter and wash four times by decantation with 50-ml portions of hot water containing a few drops of sulfuric acid. Finally transfer the precipitate to the filter and wash with hot water till free from acid. Ignite the wet precipitate and filter in a platinum or porcelain crucible. Do not heat over the blast lamp

or Méker burner, because barium sulfate is decomposed at about 900°. Cool in a desiccator and weigh as $BaSO_4$.

The precipitate usually contains a little chloride and the results are likely to be a little low. Sometimes a low result is caused by too rapid combustion of the filter which causes the formation of barium sulfide. To correct both of these errors, moisten the precipitate with a few drops of 18 N sulfuric acid, carefully evaporate off the acid, gently ignite, and weigh again. Repeat the treatment until two successive weighings agree within 0.3 mg.

Remark. — It is difficult to get pure precipitates of barium sulfate.* One liter of pure water dissolves only about 3 mg of barium sulfate, and it is even less soluble in water containing a little sulfuric acid. It is appreciably soluble in solutions containing more than 1 ml of 6 N mineral acid per 100 ml and is very soluble in concentrated sulfuric acid. A full discussion of the problem of producing pure precipitates of barium sulfate is given under Sulfuric Acid.

The formation of a little barium sulfide during the ignition of the precipitate does not usually cause error, for it is easily roasted back to sulfate by heating the inclined crucible with a small flame at the back so that there is ready access of air into the crucible.

2. Determination of Barium as Chromate

Dilute the neutral solution, containing not more than 0.4 g of barium, to 200 ml, add 10 drops of 6 N acetic acid, heat to boiling, and slowly add a slight excess of ammonium chromate solution. Prepare the reagent by dissolving 12.5 g of ammonium dichromate in 100 ml of water and adding ammonium hydroxide until the color is a clear yellow. Allow the precipitate of barium chromate to settle, and make sure that the precipitation is complete by adding a little more reagent. When cold, filter through a Gooch or Munroe crucible and wash with hot water until 20 drops of the filtrate give scarcely any reddish brown coloration with a neutral solution of silver nitrate. Dry the precipitate in the hot closet, and then heat within a larger porcelain crucible (cf. p. 37) until the precipitate becomes a bright yellow.† Cool and weigh as $BaCrO_4$.

Solubility of Barium Chromate‡

87,000 ml of water at ordinary temperatures dissolve 1 g $BaCrO_4$.
23,000 ml of boiling water dissolve 1 g $BaCrO_4$.

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* Cf. M. J. van't Krys, *Z. anal. Chem.*, **1910**, 393.

† Often some of the precipitate is reduced to chromic oxide by traces of organic matter, whereby it appears slightly greenish. By long-continued ignition in an open crucible, the chromic oxide is changed back to chromate, and the precipitate appears a homogeneous yellow throughout.

‡ P. Schweizer, *Z. anal. Chem.*, **1890**, p. 414, and R. Fresenius, *ibid.*, **1890**, p. 418.

50,000 ml of a 0.75 per cent ammonium acetate solution (at 15°) dissolve 1 g $BaCrO_4$.
45,000 ml of a 0.5 per cent ammonium nitrate solution (at 14°) dissolve 1 g $BaCrO_4$.
24,000 ml of a 1.5 per cent ammonium acetate solution (at 15°) dissolve 1 g $BaCrO_4$.
23,000 ml of 0.5 per cent ammonium nitrate solution dissolve 1 g BaCrO.
3,700 ml of 1 per cent acetic acid solution dissolve 1 g $BaCrO_4$.
2,600 " 5 " " ..
2,000 " 10 .. 1 " "
1,800 " 10 chromic acid solution dissolve 1 g $BaCrO_4$.

The solubility of barium chromate, therefore, increases considerably with increasing concentrations of either acetic or chromic acid; the solubility is affected to a much less degree by solutions containing neutral ammonium salts. By the additions of small amounts of neutral ammonium chromate the solubility becomes much less.

Separation of the Alkaline Earths from Magnesium and from the Alkalies

I. Separation of Calcium from Magnesium (and Alkalies)

The separation of calcium from magnesium depends upon the different solubilities of the two oxalates. Calcium oxalate is practically insoluble in hot water, whereas magnesium oxalate is fairly soluble; 1500 ml of cold water, or 1300 ml of boiling water, dissolve 1 g of $MgC_2O_4 \cdot 2H_2O$. The latter is more soluble in ammonium chloride solutions and much more soluble in the presence of a large excess of ammonium oxalate; 20 g of ammonium oxalate will prevent the precipitation of 2.7 g of magnesium chloride in 100 ml of solution.*

It has been known for a long time that, when calcium oxalate is precipitated in the presence of magnesium ions, particularly when the solution has remained for a long time in contact with the precipitate, some magnesium is likely to be found in the precipitate. This has been attributed to the formation of a solid solution of magnesium oxalate in calcium oxalate, to adsorption or occlusion of magnesium oxalate,† or to the gradual breaking down of a supersaturated solution of magnesium oxalate.‡ For this reason it is quite generally believed that a precipitate of calcium oxalate formed in the presence of magnesium ions is rarely, if ever, pure,§ and hence it is customary to filter off the precipitate, redissolve it in acid, and reprecipitate whenever the content of magnesium amounts to more than a few milligrams. Bach and W. Fresenius,|| however, have apparently proved that Richards¶ was right in asserting that the separation is accurate if the proper conditions are maintained.

For the precipitation of small quantities of calcium in the presence of much magnesium, three methods have been proposed. (1) The calcium oxalate is formed in the usual way, the precipitate is filtered off, dissolved, and reprecipitated a second and a third time. (2) The calcium oxalate is precipitated in the presence of ammo-

* Bobtelsky and Malkowa-Janowski, *Z. angew. Chem.*, **40**, 1437 (1927).
† T. W. Richards, *Z. anorg. Chem.*, **28**, 701 (1901).
‡ W. M. Fischer, *Z. anal. Chem.*, **153**, 62 (1926).
§ Cf. Lundell and Knowles, *J. Am. Ceramic Soc.*, **10**, 834 (1927).
|| *Chem. Ztg.*, **49**, 514 (1926).
¶ *Loc. cit.*

nium salt using only a slight excess of ammonium oxalate over that required by the calcium. (3) The calcium oxalate is precipitated in 100 ml of solution by the addition of 20 g of ammonium oxalate; the hot solution is filtered after standing a short time and no attention paid to any precipitate of magnesium oxalate that forms slowly in the cold. When the last method is used, the excess ammonium salts must be removed before attempting to precipitate .

Procedure. — Dilute the slightly acid solution with hot water so that not more than 0.3 g of either calcium or magnesium is present in 300 ml. Add 10 g of ammonium chloride, if not already present, heat to 80°–90° and slowly add, while stirring, an aqueous solution of 2 g of $(NH_4)_2C_2O_4 \cdot H_2O$. Add ammonium hydroxide until the solution is slightly ammoniacal and allow the solution to stand an hour, but not much longer, before filtering. Filter, wash with hot water and continue as described under Calcium.

Determination of Calcium and Magnesium in Limestone and Dolomite

Limestone is impure, native calcium carbonate. Dolomite is an isomorphous mixture of calcium and magnesium carbonates. Samples of limestone and dolomite usually contain small quantities of ferrous and manganous carbonates and a little silica or silicate. For most purposes, it is desired to know the calcium and magnesium present as carbonates rather than the total calcium and magnesium. In other words, a commercial analysis would not take into consideration any calcium or magnesium present in the residue insoluble in acid.

Dissolving the Sample. — Weigh out duplicate portions of about 1 g of the finely ground and well-mixed sample into 250-ml casseroles. Moisten the powder with 5 ml of water, cover the casserole with a watch glass, and add 10 ml of $6N$ HCl in small portions. When effervescence has ceased, wash off the bottom of the cover glass, raise it a little by means of a glass triangle and evaporate to dryness on the water-bath. Heat the residue in the hot closet at 120° for 1 hour to dehydrate thoroughly any silica that may be present. Moisten the residue with 10 ml of $6N$ hydrochloric acid and warm gently. Dilute with about 30 ml of water, heat to boiling, and filter off the insoluble, siliceous residue. Wash the residue twice with 5-ml portions of hot, $2N$ hydrochloric acid and then with hot water till free from chloride. The residue may be ignited and weighed if it is desired to know the amount of insoluble residue.

Precipitation of Iron, Aluminum, and Manganese. — To the filtrate and washings add bromine water until a slight excess is present as shown by the color of the solution. Boil and add $6N$ ammonia solu-

tion until a slight ammoniacal odor persists after blowing away the vapors. Heat again just to boiling and promptly filter off the precipitate of $Fe(OH)_3$, $Al(OH)_3$, and $MnO_2 \cdot H_2O$. Wash the precipitate 6 times with small portions of hot water. Reserve the filtrate for the calcium and magnesium determinations.

Sometimes the precipitate contains a little calcium carbonate from the carbon dioxide in the air and often a little magnesium hydroxide. Wash the precipitate back into the casserole, place the casserole under the funnel, pour 5 ml of hot, $3\,N$ hydrochloric acid on the upper edge of the filter, and wash the filter with a little hot water. Continue the treatment with acid and water until all the precipitate left on the filter is dissolved. Finally wash the filter with a little dilute ammonia. Precipitate with bromine water and ammonia just as before, filter through the original filter, and wash this second precipitate till free from chloride.*

Make the combined filtrate acid with acetic acid, bring to a volume of about 300 ml, add 10 g of ammonium chloride dissolved in a little water, heat to 80°–90°, and slowly add, while stirring, 60 ml of hot, $0.5\,N$ ammonium oxalate solution. Add ammonium hydroxide until the solution is slightly ammoniacal and allow the precipitate to stand an hour, but not much longer, before filtering. Filter into a weighed Gooch crucible, wash with hot water until free from halide, dry at 100°–105°, and weigh as $CaC_2O_4 \cdot H_2O$.†

Make the filtrate acid with hydrochloric acid, concentrate to about 300 ml, add 5 g of ammonium acetate dissolved in a little water and 20 ml of N $(NH_4)_2HPO_4$ solution. Heat to near the boiling point and continue as described on p. 80.

II. Separation of Strontium from Magnesium

This separation finds practical application in the analysis of almost all mineral waters and of minerals containing strontium. In all these cases, however, strontium occurs in relatively small amounts in the presence of large amounts of calcium and varying amounts of magnesium, so that it is a question, first, of separating

* The manganese content of limestone is low. If the treatment with bromine is omitted, practically all the manganese will pass into the filtrate and will probably be precipitated with the magnesium, although manganese ammonium phosphate forms very slowly in strongly ammoniacal solution. If much manganese is present it is best to precipitate the iron and aluminum by the basic acetate method and the manganese in the filtrate as sulfide. Concerning the precipitation of manganese by ammonia and bromine as well as the oxidation of ammonia and ammonium salts by bromine, see Manganese, p. 137.

† One of the other methods described under Calcium can be used. Ignition to oxide is probably the most reliable but it involves the use of a platinum crucible.

calcium and strontium from magnesium. This separation is effected by the precipitation of the calcium and strontium as oxalates as described on p. 85.

The filtrate containing magnesium may also contain traces of strontium. Remove ammonium salts by evaporating to dryness and heating the residue, dissolve this in hydrochloric acid, add sulfuric acid and alcohol, and allow the solution to stand for 12 hours. Filter off any resulting precipitate, consisting of strontium or barium sulfate, and weigh. From this filtrate precipitate the magnesium as magnesium ammonium phosphate as described on pp. 80 or 81, and weigh as the pyrophosphate.

III. Separation of Barium from Magnesium

If it is desired to separate only barium from magnesium, make the solution (which must be free from nitric acid) acid with hydrochloric acid, heat to boiling, and precipitate the barium by the addition of boiling, dilute sulfuric acid (cf. p. 88). Precipitate the magnesium in the filtrate as magnesium ammonium phosphate in the usual way.

In most cases, however, a separation of barium, strontium, and calcium from the magnesium is involved. Precipitate the three alkaline earths as oxalates as described for the separation of calcium from magnesium. A few milligrams of barium will escape precipitation. To recover this, add a little ammonium sulfate to the hot solution, filter, wash, and weigh as $BaSO_4$. In the filtrate, determine the magnesium as pyrophosphate (p. 79).

IV. Separation of the Alkaline Earths from One Another

Principle. — The mixture of the dry nitrates is treated with ether-alcohol, which dissolves calcium nitrate alone. The residue is taken up in water, the barium is precipitated as chromate, and the strontium is determined in the filtrate as sulfate.

PROCEDURE

(*a*) Separation of Calcium from Strontium and Barium according to Rose-Stromeyer-Fresenius

The three metals are assumed to be present together in solution in the form of their nitrates. Evaporate the solution in a small Erlenmeyer flask, as described under Lithium, p. 71, while passing a stream of dry, warm air through the flask. When all the water is evaporated, raise the temperature of the oil-bath to 140° and maintain this temperature for 1 to 2 hours, still passing the current of warm air through the flask. Cool, treat the dry residue with 10 times its weight of absolute alcohol, stopper the flask, and allow it to stand with frequent shaking for 1 to 2 hours. Add an equal volume of ether, close the flask, shake, and allow it to stand 12 hours. Filter through a filter moistened with ether-alcohol and wash with ether-alcohol until a few drops of the filtrate evaporated on platinum-foil leave no residue.

Evaporate the filtrate to dryness on a lukewarm water-bath, dissolve

the calcium nitrate in water, precipitate as the oxalate, and, after ignition, weigh as the oxide.

Remark. — If only a small amount of calcium is present (not more than about 0.5 g) the above separation is complete. With large amounts of calcium, the residue of strontium and barium nitrates almost always contains some calcium. In this case evaporate the aqueous solution again to dryness in the same way as before and repeat the treatment with alcohol and ether. Determine the calcium in the combined filtrates.

(*b*) Separation of Barium from Strontium according to Fresenius*

Requirements. — 1. Ammonium dichromate solution. Dissolve 100 g of ammonium dichromate (free from sulfate) in 500 ml of water, add 135 ml of 6 *N* ammonium hydroxide solution, filter if necessary, and dilute to 1 l.

2. Ammonium acetate solution. Dissolve 231 g in 1 l of water, or mix equal volumes of 6 *N* acetic acid and 6 *N* ammonia, leaving the solution slightly ammoniacal rather than acid.

3. Acetic acid, 6 *N*.

4. Nitric acid, 2 *N*.

Procedure. — Dissolve the residue of strontium and barium nitrates obtained after the above treatment with ether-alcohol in a little water and dilute the solution until the concentration corresponds to about 1 g of mixed nitrates in 300 ml, heat to boiling, add 10 drops of acetic acid and about 10 ml of ammonium chromate solution (this should be an excess over the theoretical amount necessary), and allow to stand 1 hour. Wash the precipitate of barium chromate by decantation, with water containing 25 ml of ammonium chromate solution per liter, until the wash water no longer gives a precipitate with ammonia and ammonium carbonate; then wash with hot water containing 25 ml of ammonium acetate solution per liter until the last washing gives only a slight reddish brown coloration with neutral silver nitrate solution.

The precipitate on the filter still contains a little strontium. Carefully wash it back into the vessel in which the precipitation took place, and dissolve any precipitate remaining on the filter in a little hot 2 *N* nitric acid, allowing it to run through the filter vessel containing the precipitate. Wash the filter with hot water till free from acid. Heat the precipitate till it dissolves in the dilute nitric acid (about 6 ml is usually sufficient). Dilute the solution to 200 ml, heat to boiling, add 5 ml of ammonium acetate solution, little by little, and finally enough ammonium chromate solution to cause the disappearance of the odor of acetic acid from the solution (usually about 10 ml is necessary). After it has stood for 1 hour pour the liquid through a Gooch

anal *Chem.*, **29**, 427 (1890); **44**, 742 (1906).

crucible, cover the residue in the dish with hot water, allow to cool, filter and wash with cold water until the filtrate gives only a slight opalescence with neutral silver nitrate. Dry the precipitate, ignite gently in an air-bath (cf. p. 37), and weigh as $BaCrO_4$.

Add 1 ml of 6 N nitric acid to the filtrate, concentrate somewhat, and precipitate the strontium as carbonate by the addition of ammonia and ammonium carbonate. The precipitate always contains some strontium chromate. Wash it once with hot water, dissolve in hydrochloric acid, and determine the strontium as sulfate, according to p. 87.

The results obtained according to this method are very satisfactory.

METALS OF GROUP III

ALUMINUM, CHROMIUM, TITANIUM, IRON, URANIUM, NICKEL, COBALT, ZINC, AND MANGANESE

A. DIVISION OF THE SESQUIOXIDES

ALUMINUM, CHROMIUM, IRON, TITANIUM, AND URANIUM

Aluminum, Al. At. Wt. 26.97

Forms: Al_2O_3, $AlPO_4$, $Al(C_9H_6ON)_3$

1. Determination as Al_2O_3

To determine aluminum as oxide, it is precipitated as the hydrated oxide which, as van Bemmelen has shown, is really $Al_2O_3 \cdot xH_2O$ rather than the hypothetical $Al(OH)_3$.

The hydrated oxide is amphoteric and also tends to form colloidal solutions. Because of its amphoteric nature it is best precipitated, as Blum* has shown, by keeping the hydrogen-ion concentration at about 10^{-7}, as it is in pure water. Because of the colloidal nature of the precipitate it is advisable to have ammonium salt in the solution and to wash the precipitate with water containing ammonium salt. The ammonium salt also prevents the precipitation of magnesium hydroxide by repressing the ionization of ammonium hydroxide.

Procedure. — To the solution containing at least 5 g of ammonium chloride per 200 ml, or an equivalent quantity of hydrochloric acid, add a few drops of methyl red indicator (0.2 per cent alcoholic solution) and heat just to boiling. Add 6 N ammonium hydroxide until the color of the solution changes to a distinct yellow. Boil for 2 minutes and filter promptly. Wash the precipitate thoroughly with hot, 2 per cent ammonium nitrate solution. Ignite in an open crucible, cool and weigh as Al_2O_3.

* *J. Am. Chem. Soc.*, **38**, 1282 (1916).

The ammonia should be freshly distilled. When kept for any length of time in glass bottles it invariably contains a little dissolved silica which precipitates when the ammonia is neutralized. Because of the solvent effect of acids and bases on glass, only glass of the boro-silicate type should be used in the chemical laboratory.

According to Britton, aluminum hydroxide begins to precipitate at $p_H = 4.14$ and the precipitate is dissolved at $p_H = 10.8$. The above treatment with ammonium hydroxide serves to keep the p_H within these limits; methyl red changes color at $p_H = 4.4 - 6.0$. Most separations of aluminum from other metal ions are based upon the regulation of the p_H. A salt of a weak acid added to the aqueous solution of an aluminum salt will serve to react with H^+ produced by hydrolysis and thus favor the completion of the reaction. The reaction is also helped if the weak acid is unstable and breaks down as fast as it is formed because, in accordance with the mass-action law, a reaction is favored by the removal of any product produced. Chancel* recommended sodium thiosulfate as a suitable salt:

$$2\,Al^{+++}$$ [illegible]

Procedure. — Add to the dilute, neutral solution (about 0.1 g Al in 200 ml) an excess of sodium thiosulfate and boil until all traces of SO_2 are expelled. Add 6 N ammonium hydroxide† until its odor is barely perceptible after blowing away the vapors, and continue boiling a little longer. Filter off the precipitate of $Al(OH)_3$ and S, wash it with hot 2 per cent ammonium nitrate solution, and ignite in a porcelain crucible. Such a precipitate of hydrated Al_2O_3 is much denser than that produced by direct precipitation with ammonia and it is very easy to filter and wash.

Alfred Stock‡ accomplished the same thing by adding a mixture of potassium iodate and iodide. The reaction

[illegible] $$+ 6\,H^+ = 3\,H_2O + 3\,I_2$$

is very sensitive to hydrogen ions, and, moreover, the free iodine can be removed easily by adding sodium thiosulfate

$$I_2 + 2\,S_2O_3^{--} = S_4O_6^{--} + 2\,I^-$$

Stock's procedure is as follows:

Procedure. — The solution in which the aluminum is to be determined should be very slightly acid; if more acid is present add sodium hydroxide solution until a slight permanent precipitate is obtained. Redissolve by means of a few drops of hydrochloric acid. Add equal volumes of a 25 per cent potassium iodide solution and a saturated potas-

* *Compt. rend.*, **46**, 987; *Z. anal. Chem.*, **3**, 391.

† If the addition of ammonia is omitted, the solution will retain traces of aluminum.

‡ Ber., **1900**, 548.

sium iodate solution (about 7 per cent KIO_3). After about 5 minutes, decolorize the solution by the addition of a 20 per cent sodium thiosulfate solution and add a little more of the potassium iodide and iodate mixture to make sure that enough is present. Add 1 or 2 ml more of sodium thiosulfate solution and heat the mixture half an hour on the water-bath. The pure white precipitate settles out well, and can be filtered through a filter with relatively wide pores, washed with hot 2 per cent ammonium nitrate solution, ignited and weighed as Al_2O_3.

Remark. — The presence of calcium, magnesium, or boric acid does not interfere with the above determination, but if phosphoric acid is present, aluminum phosphate is precipitated. It is obvious that the method cannot be employed in the presence of organic substances such as tartaric acid, citric acid, sugar, etc., which prevent the precipitation of hydrated alumina.

Wynkoop* and Schirm† used ammonium nitrite as a suitable salt of a weak acid.

$$2\,Al^{+++} + 6\,H_2O \rightarrow 2\,Al(OH)_3 + 6\,H^+$$
$$6\,H^+ + 6\,NO_2^- \rightarrow 6\,HNO_2 \qquad 6\,HNO_2 \rightarrow 3\,H_2O + 3\,NO + 3\,NO_2$$

Procedure. — If the solution is acid, add ammonia until the precipitate first formed dissolves only slowly on stirring. Add an excess of a 6 per cent solution of pure ammonium nitrite,‡ dilute the solution to 250 ml, and boil until no more fumes of nitrous oxides are evolved (about 20 minutes). Filter off the precipitate, wash with hot 2 per cent ammonium nitrate solution, ignite wet in a platinum crucible, and weigh as Al_2O_3.

Remark. — In the presence of more than 1 per cent of ammonium salts, these are hydrolyzed enough so that the solution remains acid and the precipitation of the aluminum is incomplete even after long boiling. In such cases it is necessary to add some NH_4OH to accomplish complete precipitation.

2. Determination as $AlPO_4$

If a solution containing Al^{+++}, alkaline-earth ion, and phosphoric acid is carefully neutralized, $AlPO_4$ will form before $Al(OH)_3$ or alkaline-earth phosphate. If, however, the p_H is raised a little higher, the precipitate is likely to become one of alkaline-earth phosphate and $Al(OH)_3$. In the ferric state iron behaves like aluminum and in the ferrous state like alkaline earth.

It is quite common practice to determine aluminum in the presence of iron by reducing the iron to the ferrous state by sulfurous acid or sodium thiosulfate, adding ammonium phosphate, and then continuing the treatment with sodium thiosulfate as in the method of Chancel described above. The results are not entirely satisfactory, but Lundell and Knowles§ have shown that the determination of small

* *J. Am. Chem. Soc.*, **19**, 434 (1897).

† *Chem. Ztg.*, **1909**, 877.

‡ Sometimes the reagent contains a little barium which should be precipitated with ammonium sulfate before using it in an analysis.

§ *J. Am. Chem. Soc.*, **14**, 1136 (1922).

quantities of aluminum as phosphate can give very accurate and reproducible results. Their procedure is as follows:

To 400 ml of a solution containing sufficient acid to make it 0.3N in HCl, add 1 g of $(NH_4)_2HPO_4$, or more if this does not provide a tenfold excess. Prepare some macerated filter pulp by tearing up ashless filter paper into small pieces and shaking the paper in a stoppered flask with a little water until a creamy emulsion is obtained. Add some of this paper pulp to the solution to aid in the filtration of the $AlPO_4$ precipitate. Add a few drops of methyl orange indicator solution and enough ammonium hydroxide to make the color of the stirred solution yellow. Then make acid with 1 ml of 6N HCl, heat to boiling, and to the boiling solution add 30 ml of 25 per cent ammonium acetate solution. Boil 5 minutes, filter and wash the precipitate with 5 per cent ammonium nitrate solution until it is practically free from chloride. Ignite in an open porcelain crucible and weigh as $AlPO_4$.

3. Determination with 8-Hydroxyquinoline

The use of this reagent was discussed briefly under Magnesium. The aluminum salt can be formed in dilute acetic acid solutions which are buffered with ammonium acetate. The precipitate is easier to filter than is aluminum hydroxide or phosphate, and some useful separations of aluminum from other elements can be accomplished with this organic reagent.

Procedure. — Heat the solution, containing not more than the equivalent of 0.1 g Al_2O_3 and one or two drops of mineral acid per 100 ml, to about 70° and add an excess of the reagent (cf. p. 83). Slowly add 2N ammonium acetate solution until a permanent precipitate is formed, and then add 20–25 ml more. Allow the precipitate to settle, filter through a weighed Gooch crucible, wash with cold water, dry at 120–140°, and weigh as $Al(C_9H_6ON)_3$ containing 11.1 per cent of Al_2O_3.

4. Determination of Small Quantities of Aluminum

The most satisfactory test for aluminum is the formation of the red lake with aurin tricarboxylic acid, to which the trivial name *aluminon* has been given. This test (see Vol. I) can be made the basis of a colorimetric determination of aluminum by comparing the result obtained in the unknown solution with that obtained under similar conditions with known quantities of aluminum.

Aluminum is precipitated by tannin in the presence of alkali acetate as a voluminous tannin adsorption complex, and the precipitation is not prevented by tartaric acid. This procedure is described later. See Index.

IRON, Fe. At. 55.84

Forms: Ferric Oxide, Fe_2O_3, and Metallic Iron

Determination as Fe_2O_3

1. By Precipitation with Ammonia

The precipitation of ferric iron by means of ammonium hydroxide can be accomplished as described under Aluminum, but when only iron is present it is not necessary to keep the solution so near the neutral point because ferric hydroxide is not appreciably dissolved by an excess of ammonia and does not form a colloidal solution when washed with a moderate amount of hot water. The same precautions as described under Aluminum should be taken with regard to the use of freshly distilled ammonium hydroxide and the use of the best grades of glass that are not attacked to any extent by dilute bases. The precipitate is rather bulky; an ordinary 9-cm filter will hold only about 0.2 g of iron as hydrated oxide.

Procedure. — Heat the solution to about 70°, and at a volume of 200–300 ml, precipitate hydrated ferric oxide by the addition of a slight excess of $6N$ ammonium hydroxide. Allow the precipitate to settle and wash it twice by decantation with 50-ml portions of hot water. Wash with hot water or hot 2 per cent ammonium nitrate solution until free from chloride. Do not wash with ammonium chloride solution because ferric chloride is volatile upon ignition. Ignite slowly and carefully in an open porcelain or silica crucible and weigh as Fe_2O_3.

Remarks. — It is not advisable to heat the precipitate over the blast because Fe_3O_4 is formed at high temperatures. This magnetic oxide is also formed if the carbon of the filter is not consumed at a low temperature. When once formed it is very difficult to get it back to the less stable Fe_2O_3. The color of the ignited oxide does not indicate the presence of magnetite, for pure ferric oxide is nearly black after strong ignition. The ignited oxide is difficultly soluble in dilute hydrochloric acid but can be dissolved by long digestion with concentrated hydrochloric acid on the water-bath.

The formation of magnetic iron oxide during the ignition of ferric hydroxide is said to be prevented by stirring some ashless filter-paper pulp (see p. 98) into the liquid after the precipitation by ammonia.

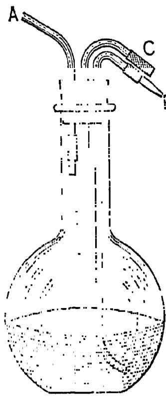

FIG. 34.

The wash-bottle shown in Fig. 34 is useful for work with hot water or with bad-smelling wash-liquids. It contains two tubes like the ordinary wash-bottle but at the end of the tube A a Bunsen valve is placed. This is made by cutting a slit in a short piece of rubber tubing, placing this on the end of the tube through which one blows in using the bottle, and sealing the other end of the rubber tubing with a piece of glass rod. On blowing the slit opens but closes to prevent escape of steam. The third tube C is closed by the finger when using the bottle or by means of rubber tubing and a pinchcock. After blowing through A, a stream of water is ejected at B if C is kept closed. When C

is opened the stream stops. It is well to wind the neck of the wash-bottle with heavy curtain cord, if it is to be used for hot water.

If the iron is in solution either as the ferrous or ferric salt of a volatile acid, it can be readily converted into ferric oxide by evaporation with sulfuric acid and ignition of the residue.

2. Determination as Metallic Iron

Iron may be determined by electrolysis, but this method offers no advantages over the gravimetric method just described or the following volumetric process.

In the analysis of oxidic iron ores or of mixtures of considerable iron oxide with comparatively little alumina, titanium dioxide, or silica, the following method is accurate and rapid.*

Weigh the finely powdered† substance in a procelain boat. Introduce the boat into a tube of difficultly fusible glass and heat to redness in a stream of dry hydrogen until no more drops of water condense on the cool, front end of the tube, and the contents of the boat appear gray and not black. By this means the ferric oxide is reduced to metallic iron:

$$Fe_2O_3 + 3\ H_2 = 3\ H_2O + 2\ Fe$$

After cooling in the stream of hydrogen, again weigh the boat and its contents after they have remained some time in a desiccator. The loss in weight p represents the amount of oxygen originally combined with the iron, from which the amount of iron can be calculated:

$$\frac{2\ Fe}{3\ O} = 2.326\ p = \text{weight of iron}$$

Remark. — In attempting to reduce ferric oxide to iron by means of hydrogen, it is very important to heat the oxide to bright redness. At a dull red heat, the oxide is, to be sure, reduced to metal, but in such cases black, pyrophoric iron is formed which cannot be exposed to the air and weighed without becoming oxidized. By heating to a bright red heat, however, the iron becomes gray, is no longer pyrophoric, and can, if allowed to cool in the stream of hydrogen, which is subsequently replaced by carbon dioxide, be safely weighed in the air without fear of oxidation.

Although this method is extremely simple, and the corresponding oxides of aluminum, chromium, titanium and zircon, etc., are not reduced under the same conditions, it should be used with caution and only when the ferric oxide greatly predominates in a mixture of oxides. Otherwise the reduction of the iron is incomplete on account of some of the ferric oxide being enclosed within the particles of

* Rivot, *Ann. chim. phys.*, [3] **30**, 188 (1850); *Liebig's Ann.*, **78**, 211 (185).

† Ferric oxide after having been powdered and ignited is so hygroscopic that the porcelain boat should be placed within a weighing-beaker with ground-glass top immediately after removing it from the desiccator, and then weighed.

foreign oxide. This has been proved by the work of Daniel and Leberle* and by Treadwell and Wegelin. Moreover, the above computation shows that the error in determining the weight of reduced iron is multiplied by 2.33 in the computed weight of iron.

It is more accurate to dissolve the metallic iron in dilute sulfuric acid out of contact with the air and determine the amount present volumetrically by titrating with potassium permanganate solution.

3. Volumetric Determination of Iron according to Marguerittet†

Although the volumetric methods are discussed in the second part of this book, this determination is so important and is so often used to test the purity of the iron oxide produced by a gravimetric analysis that it seems proper to discuss it at this place.

Principle of the Method

Ferrous salts are oxidized by potassium permanganate in acid solution to ferric salts:

$$2\,KMnO_4 + 10\,FeSO_4 + 8\,H_2SO_4 = K_2SO_4 + 2\,MnSO_4 + 8\,H_2O + 5\,Fe_2(SO_4)_3$$

If, therefore, a potassium permanganate solution of known strength is slowly added to the solution of a ferrous salt, it will be decolorized as long as there remains ferrous salt to react with it. As soon as all the ferrous salt has been oxidized, the next drop of the permanganate will impart a permanent pink color to the solution, whereby the *end point* of the reaction is determined.

Preparation and Standardization of the Permanganate Solution

The concentrations of the standard solutions used in volumetric analysis are usually referred to the so-called *normal* concentration. A *normal* solution is one that contains *one equivalent weight in grams per liter*. It has been assumed throughout this volume that the abbreviation N signifies a concentration of one equivalent weight in grams per liter, that $6\,N$ represents a solution 6 times as strong, and $0.1\,N$ represents a concentration of one-tenth an equivalent weight in grams per liter.

An equivalent weight of a salt *as precipitant* is determined by the valence of the characteristic ion. Thus the molecular weights of NaCl, $AgNO_3$ and KCNS and one-half the molecular weights of $BaCl_2$, $(NH_4)_2CO_3$, and $CaCO_3$ are equivalent weights.

An equivalent weight of an *acid* is determined by the number of replaceable hydrogen atoms in the molecule and of a base by the number of replaceable hydroxyl ions. Thus the molecular weights of HCl, HNO_3, KOH, and NH_4OH, and one-half the molecular weights of H_2SO_4, and $Ba(OH)_2$, are equivalent weights.

As an *oxidant* or as a *reductant* the equivalent weight is determined by the *change*

* *Z. anorg. Chem.*, **34**, 393 (1903).

† *Ann chim. phys.*, [3] **18**, 244 (1846).

in valence which takes place when the reaction of oxidation and reduction occurs. Thus, in the above equation which may also be expressed as follows:

$$MnO_4^- + 5\ Fe^{++} + 8\ H^+ \rightarrow Mn^{++} + 5\ Fe^{+++} + 4\ H_2O$$

the manganese is reduced from a valence of seven in permanganate to a valence of two in the manganous salt while the iron is changed from a valence of two to a valence of three.

Therefore, in the oxidation of a ferrous salt by permanganate the equivalent weight of permanganate is one-fifth the molecular weight, and the equivalent weight of the ferrous salt is that weight which contains an atomic weight in grams of iron.

For titrations with permanganate a tenth-normal solution is commonly used. To make 0.1 *N* $KMnO_4$ solution take one-fiftieth of the molecular weight in grams, or 3.161 g of $KMnO_4$, and dilute to 1 liter.

Although it is possible to purchase very pure potassium permanganate, it is not advisable to take the trouble of weighing out just this amount of the substance and dissolving it in exactly enough water, for the distilled water in which the permanganate is dissolved almost always contains traces of organic matter oxidizable by the permanganate. Consequently it is better to weigh out on a watch glass approximately 3.2 g of permanganate, dissolve it in a liter of water, boil 10–15 minutes, allow to cool over night, and then filter through asbestos.* After this time all the oxidizable matter in the water will have been completely destroyed. Filter the solution through an asbestos filter and then standardize. The addition of 10 g of KOH per liter increases the stability of the solution.

Standardization of the Potassium Permanganate Solution

It is possible to standardize a solution of permanganate by a number of different methods. In this case the most natural way would seem to be to take a sample of pure ferrous salt or to make a ferrous solution from a weight of pure iron. Owing to the difficulty in procuring a sample of perfectly pure ferrous salt or of perfectly pure iron, it is generally considered better to standardize against pure sodium oxalate. Specially purified sodium oxalate can now be purchased from dealers in chemicals and can also be obtained from the United States Bureau of Standards at Washington, D. C.

Procedure. — In a 400-ml beaker, dissolve 0.25–0.3 g of sodium oxalate in 200–250 ml of hot water (80–90°) and add 10 ml of 18 *N* sulfuric acid.† Titrate at once with 0.1 *N* $KMnO_4$ solution, *stirring the liquid vigorously and continuously.* The permanganate must not be added more rapidly than 10–15 ml per minute, and the last 0.5–1 ml must be added dropwise with particular care to allow each drop to be fully decolorized before the next is introduced. The excess of permanganate used to cause an end-point color should be estimated by matching the color in another beaker containing the same bulk of acid and hot water. The temperature of the solution should not be below 60° by the time the

* Cf. Morse, Hopkins, and Walker, *Am. Chem. J.*, **18** (1896), p. 401.

† The reaction starts more quickly if 10 ml of $MnSO_4$ titrating solution is used instead of the 18 *N* H_2SO_4 (see Zimmermann-Reinhardt method in Part II.

end point is reached; more rapid cooling may be prevented by allowing the beaker to stand on a small asbestos-covered hot plate during the titration. The use of a small thermometer as stirring-rod is most convenient in these titrations, as the variation of temperature is then easily observed.

To compute the normal concentration of the permanganate, first find the weight of sodium oxalate oxidized by 1 ml of permanganate by dividing the weight taken by the number of milliliters of permanganate used. From the reaction

$$2\,MnO_4^- + 5\,C_2O_4^{--} + 16\,H^+ \rightarrow 2\,Mn^{++} + 10\,CO_2 \uparrow + 8\,H_2O$$

it is evident that the equivalent weight of sodium oxalate is one-half the molecular weight, or 67.00. One liter of normal permanganate, therefore, would oxidize 67 g of sodium oxalate, and 1 ml would oxidize 0.067 g of $Na_2C_2O_4$. To find the normal concentration of the permanganate, divide the weight oxidized by 1 ml of permanganate solution by the milli-equivalent, 0.067, of sodium oxalate.

Thus if a grams of pure $Na_2C_2O_4$ reacted with t milliliters of the given permanganate, then $\frac{a}{t \times 0.067}$ is the normal concentration or *normality* of the permanganate. To find the weight of any other substance which reacts similarly with 1 ml of the permanganate multiply the normality of the permanganate solution by the milli-equivalent of the substance. Thus, as the milli-equivalent of iron when it is oxidized by permanganate from the ferrous to ferric condition is 0.05584 g, then using the above notation,

$$1 \text{ ml of } \frac{a}{t \times 0.067} N\ KMnO_4 = \frac{a \times 0.05584}{t \times 0.067} \text{ g of Fe}$$

Analysis of Ferric Compounds according to the Method of Margueritte

From what has already been said, it is evident that in order to determine the amount of iron present in a solution by titration with potassium permanganate, it is necessary for the iron to be present entirely in the ferrous condition. To apply this method therefore to the analysis of ferric compounds, it is first necessary to reduce them completely.

*Procedure.** — Transfer the solution to a 200-ml flask (K, Fig. 35) which is fitted with a rubber stopper carrying glass tubes for the entrance and exit of gas. The volume of the solution should be approximately 100 ml and it should not contain more than 0.15 g of iron. Add 5 ml of 18 N sulfuric acid and introduce hydrogen sulfide gas into the cold solution for 30 minutes and for 15 minutes as it is slowly heated to boiling. Then add 15 ml more of 18 N sulfuric acid and continue the gentle boiling for at least 30 minutes, while a stream of carbon dioxide is bubbled through the solution. In the train shown in Fig. 35, the bottle A contains water, the bottle B a fairly strong solution of per-

* The conditions given in these directions are those recommended by Lundell and Knowles, *J. Am. Chem. Soc.*, **43**, 1565 (1921).

manganate, and the tower *C* pumice wet with copper sulfate solution. In this way all hydrogen sulfide or other reducing gas is removed from the carbon dioxide. After all the excess hydrogen sulfide has been removed and the volume of the solution reduced to about 50 ml, allow

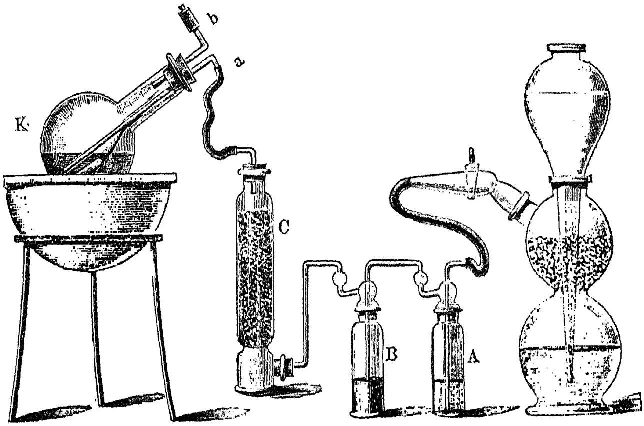

FIG. 35.

the solution to cool while the stream of carbon dioxide is still passing. Dilute with 200 ml of cold water and titrate with standard permanganate solution.

The precipitate of sulfur formed during the reduction of the ferric salt by the hydrogen sulfide does no harm if the above directions are followed closely. If it is desired to remove any precipitated sulfide, the solution should be filtered before the last addition of acid and the filtrate given a further, short treatment with hydrogen sulfide.

If t milliliters of permanganate were necessary to oxidize the solution completely and 1 ml of the permanganate corresponds to a grams of iron, then the titrated solution evidently contains $a \cdot t$ grams of iron.

Besides hydrogen sulfide, a great many other substances can be used to reduce the ferric salt, *e.g.*, zinc, sulfurous acid, stannous chloride. The use of these substances will be discussed in the portion of this book devoted to Volumetric Analysis.

Remark. — The titration of a solution by means of potassium permanganate takes place preferably in a sulfuric acid solution; with hydrochloric acid too high results will be obtained (owing to the fact that the permanganate oxidizes some of the acid), unless the oxidation takes place in a dilute solution in the presence of a large excess of manganous sulfate. See Volumetric Analysis.

Determination of Iron and Sulfur in Ferrous Ammonium Sulfate

The determination of iron is one of the best known of all the gravimetric methods of analysis and for many years it has been the custom to require most students of analytical chemistry in the colleges of the United States to carry out an analysis of ferrous sulfate or of ferrous ammonium sulfate. In a sulfate solution, some basic ferric sulfate is often formed if the precipitation of ferric hydroxide is accomplished by merely neutralizing with ammonia. It is the general practice, therefore, to dissolve the first precipitate in acid and repeat the precipitation with ammonia.

It has been shown, however, that the formation of basic sulfate can be prevented if a considerable excess of ammonium hydroxide is used.

Procedure. — Weigh out, to the nearest milligram, duplicate portions of about 1 g into 400-ml beakers. Moisten the sample with 5 ml of $6\,N$ hydrochloric acid, dilute with 5 ml of water, and heat, if necessary, to dissolve the sample. Heat nearly to boiling, and to the hot solution add concentrated nitric acid, drop by drop, until all the iron is oxidized to the ferric condition. When the iron is partially oxidized, the nitric oxide combines with the excess of ferrous salt, forming a dark brown, unstable compound. Continue adding the nitric acid until the dark color fades and a clear yellow solution is obtained. Not more than 2 ml of nitric acid should be necessary.* Boil gently for about 3 minutes to remove the reduced nitrous compounds. Dilute to about 200 ml and neutralize with ammonium hydroxide, finally adding 5–7 ml of concentrated ammonium hydroxide in excess. Heat carefully to about 70° and allow the precipitate to settle. Filter through a filter that has an ash of less than 0.1 mg, wash the precipitate twice by decantation with 50-ml portions of hot water, and finally with hot water from the wash bottle until free from chloride. Ignite slowly and carefully in an open porcelain or platinum crucible and weigh as Fe_2O_3. Report the percentage of iron present in the sample.

Dilute the filtrate to about 400 ml, neutralize with hydrochloric acid, and add 25 milli-equivalents in excess. Heat to boiling and precipitate the sulfate as described under Sulfuric Acid (Hintz and Weber).

Titanium, Ti. At. Wt. 47.90

Titanium occurs very commonly in rocks but usually only in small quantities. It occurs together with zirconium, cerium, and thorium and is very similar to zirconium in its chemical behavior.

For the determination of small quantities of titanium the colorimetric method is very satisfactory except when large quantities of iron, phos-

* Bromine or hydrogen peroxide can be used instead of nitric acid. If a black iron precipitate is obtained later, owing to incomplete oxidation, add 10 ml of 3 per cent hydrogen peroxide and heat till the precipitate is reddish brown.

phorus, alkali salts, or even traces of vanadium are present. When these elements interfere it is not advisable to try the colorimetric determination until after they have been removed.

When titanium is unaccompanied by other cations of this group it is best to precipitate it with ammonia. The precipitate of $Ti(OH)_4$, or hydrated TiO_2, is not dissolved by an excess of ammonia and is easily converted into TiO_2 by ignition.

Usually it is necessary to remove titanium from interfering elements, and then, after the separation has been accomplished, it is best to determine the titanium volumetrically or colorimetrically.

In Schoeller and Powell's method (see Index) titanium is precipitated as the red tannin adsorption complex from fairly acid oxalate solutions, which provides a quantitative separation from aluminum. The Gooch method depends upon adding alkali acetate and carrying out a basic acetate precipitation. The titanium precipitates in the presence of sufficient acetic acid to keep most of the aluminum in solution. The Baskerville method is based upon the fact that a nearly neutral solution of titanium and iron chlorides when boiled with sulfurous acid at moderate dilution gives a precipitate of titanium hydroxide while the iron remains in solution in the ferrous state. Thornton recommends the use of cupferron (ammonium nitrosophenylhydroxylamine). These methods will be discussed under the separations described a little farther on.

(*a*) Determination as Titanium Dioxide

Precipitate with ammonia in the manner described under Iron (p. 99) or, to the nearly neutral solution, add 10 g of ammonium acetate and 10 ml of glacial acetic acid. Dilute to about 150 ml., heat to boiling and filter. Wash the precipitate with 7 per cent acetic acid, ignite and weigh as TiO_2.

(*b*) Determination of Titanium Colorimetrically. Method of A. Weller*

(Suitable for small amounts of titanium)

This determination depends upon the fact that acid solutions of titanium sulfate are colored intensely yellow when treated with hydrogen peroxide; the yellow color increases with the amount of titanium present and is not altered by an excess of hydrogen peroxide. On the other hand, inaccurate results are obtained in the presence of hydrofluoric acid (Hillebrand); consequently it is not permissible to use hydrogen peroxide for this determination which has been prepared

* *Ber.*, **15**, 2593 (1882).

from barium peroxide by means of fluosilicic acid.* The so-called "perhydrol" is excellent though other commercial brands of hydrogen peroxide are satisfactory. Furthermore, chromic, vanadic, and molybdic acids must not be present, since they also give colorations with hydrogen peroxide. The presence of small amounts of iron does not affect the reaction, but large amounts of iron cause trouble on account of the color of the iron solution.

Alkali sulfates have a marked bleaching effect unless considerable sulfuric acid is present and even then a slight effect is noticeable.

Preparation of the Standard. — Heat 0.600 g of pure, recrystallized potassium fluortitanate, K_2TiF_6, with sulfuric acid in a platinum dish until all the fluorine is evolved. Add a little more sulfuric acid, evaporate to small volume but not to dryness, and repeat the treatment several times. Finally dilute with 5 per cent sulfuric acid to 200 ml. One milliliter of this solution corresponds to 0.001 g of TiO_2. To make sure that the standard is correct, dilute 50 ml to about 150 ml, add a slight excess of ammonia, heat nearly to boiling, filter, wash with hot water till free from potassium, ignite, and weigh as TiO_2.

Preserve the standard solution in a glass-stoppered bottle with the stopper coated with vaseline. Always withdraw the solution by means of a pipet, never by pouring it out.

In making an analysis, take 5 ml of the standard solution, mix with sufficient hydrogen peroxide to fully oxidize it (1 or 2 ml of the 3 per cent reagent), and dilute with 5 per cent sulfuric acid to 50 ml in a measuring-flask. Each cubic centimeter of this diluted standard contains 0.1 mg of TiO_2.

The Test Solution. — It is most convenient in rock analysis to determine titanium in the solution which has been used for the titration of the total iron after fusing Al_2O_3, Fe_2O_3 etc. with $K_2S_2O_7$. For accurate work, however, correction should be made for the iron and alkali content.

If necessary, evaporate the sulfate solution containing the titanium to less than 100 ml. It should contain 5 per cent or more of sulfuric acid. Add sufficient hydrogen peroxide to fully oxidize the titanium. Then, if the color is less than that of the standard, dilute to exactly

* To test for fluorine: Add a slight excess of sodium carbonate to 50 ml of the reagent and heat to decompose the peroxide. Filter if a precipitate forms and add to the boiling solution an excess of calcium chloride. Filter and ignite the precipitate. Add acetic acid till the calcium carbonate is dissolved, filter, wash, and ignite the residue gently. Test with sulfuric acid to see if a gas is evolved which will etch glass, or with sulfuric acid and silica to see if a gas is evolved which makes a drop of water turbid.

100 ml. If the color is deeper, dilute to 200 ml or until the shade is weaker than the standard. Using a colorimeter or Nessler tube, dilute 10 ml of the standard solution with 5 per cent sulfuric acid from a buret until, when viewed horizontally, the color matches that of the solution being analyzed. Repeat the comparison with several portions of the standard. Then, since the volume of the diluted standard and its titanium content are known, it is easy to compute the weight of TiO_2 per milliliter of the solution being analyzed. Thus if a milliliters of the standard (0.1 mg per ml) were diluted with b milliliters of acid to make it correspond to the color of the tested solution, of which the total volume was A milliliters, then $\frac{0.1\,a \times A}{a + b}$ = milligrams TiO_2 present.

To correct for iron, it is usually sufficient to assume that the coloring power of 0.1 g of Fe_2O_3 in 100 ml of 5 per cent sulfuric acid is about equal to 0.2 mg of TiO_2 in the same volume. It is more exact, however, to add to the standard a quantity of ferric alum solution that corresponds to the weight of iron in the sample. If A is the milliliters of the test solution used in a preliminary test, made as just described, a the milliliters of the standard used, b the milliliters of acid used, p the weight of Fe_2O_3 corresponding to the iron in A, and x the weight of iron (in terms of Fe_2O_3) which should be present in each milliliter of 5 per cent sulfuric acid used for diluting the standard, then since bx is the weight of Fe_2O_3 in $(a + b)$ milliliters of diluted standard and $\frac{p}{A}$ is the weight of Fe_2O_3 per milliliter of solution being tested, we have

$$\frac{p}{A} = \frac{bx}{a + b} \quad \text{and} \quad x = \frac{p(a + b)}{Ab}$$

To correct for the bleaching effect of alkali sulfate, a similar computation will show how much should be added to the 5 per cent sulfuric acid solution used in diluting the standard. In ordinary rock analysis, however, no correction need be applied for the alkali sulfate present if the TiO_2 content exceeds 0.02 g, when 6 g of potassium pyrosulfate is used for fusing the ignited Al_2O_3, Fe_2O_3 etc., and the melt is dissolved in 100 ml of 5 per cent sulfuric acid. If the TiO_2 content is between 0.002 and 0.01 g, the weight of TiO_2 found by the test is too low by 0.0004 g.

If vanadium is present, precipitate the titanium (and vanadium) with ammonia and fuse with sodium carbonate. Sodium vanadate is formed which dissolves in water. Sodium titanate is hydrolyzed and none of it dissolves in water. After extracting with water, therefore, fuse the residue with $K_2S_2O_7$ and dissolve the melt in 5 per cent sulfuric acid.

Considerable phosphoric acid has a bleaching effect but the quantity present in rocks is too small to be serious. It is not advisable, however, to attempt to compensate the effect of ferric sulfate by adding phosphoric acid, although this practice has been recommended.

CHROMIUM, Cr. At. Wt. 52.01

Forms: Chromic Oxide, Cr_2O_3; Barium Chromate, $BaCrO_4$

(a) *Chromic Compounds*

Determination as Chromic Oxide

1. *By Precipitation with Ammonia**

If the chromium is present in solution as chromic compound it can be precipitated exactly as described under Aluminum, by means of the slightest possible excess of ammonia† in the presence of considerable ammonium salts (or better still, by the addition of freshly prepared ammonium sulfide solution to the boiling solution). Wash the precipitated $Cr(OH)_3$ with 2 per cent ammonium nitrate solution and ignite wet in a platinum crucible. Cool and weigh as Cr_2O_3. The results obtained are always a few tenths of a per cent too high on account of the formation of small amounts of chromic chromate. It is best, therefore, to heat the precipitate and allow it to cool in a stream of hydrogen. Use a Rose crucible and introduce hydrogen from a Kipp generator. Weigh as Cr_2O_3.

If phosphoric acid is present, it will be found in the precipitate. In this case fuse the dried precipitate in a nickel crucible with sodium carbonate and sodium peroxide, whereby sodium chromate and sodium phosphate are obtained. Determine the chromate volumetrically as described for the analysis of *chromite.*

2. *By Precipitation with Potassium Iodide-Iodate Solution. Method of Stock and Massaciu*‡

Carry out the determination as with aluminum (cf. p. 96). Treat the slightly acid§ solution, contained in a porcelain dish, with a mix-

* Cf. C. Rothaug, *Z. anorg. Chem.*, **84**, 165 (1914).

† An excess of ammonia prevents the complete precipitation of the chromium hydroxide, the filtrate is then colored pink. In such cases the filtrate must be boiled until the excess of ammonia is expelled, and all the chromium is precipitated.

‡ *Ber.*, **1901**, 467.

§ If the solution is strongly acid, it is neutralized by the addition of pure KOH solution drop by drop, until a faint permanent turbidity is obtained.

ture of potassium iodide and iodate, decolorize after a few minutes by means of sodium thiosulfate solution, treat with a little more iodide and iodate and then again with a few milliliters of sodium thiosulfate, and heat half an hour on the water-bath. The flocculent precipitate of chromic hydroxide settles quickly. Filter, ignite in hydrogen, and weigh as Cr_2O_3.

3. *By Precipitation with Ammonium Nitrite**

If the solution of the chromic salt is acid, neutralize with ammonia until a slight permanent precipitate is obtained. Dissolve this precipitate with a few drops of hydrochloric acid and add an excess of 6 per cent ammonium nitrite. Boil the liquid until all nitrous fumes have been expelled. By this means practically all the chromium will have been precipitated, but in order to throw down the last traces, add ammonia, drop by drop, until the odor of free ammonia barely persists in the solution. Allow the precipitate to settle while the beaker remains on the water-bath, filter, wash with hot water, ignite wet in a platinum crucible in an atmosphere of hydrogen and weigh as Cr_2O_3.

(*b*) *Chromates*

If the chromium is present in solution in the form of an alkali chromate, free from chloride and large amounts of sulfuric acid, it may be determined very accurately by precipitation with mercurous nitrate solution as mercurous chromate; on ignition the latter is changed to Cr_2O_3.

Procedure. — To the neutral or weakly acid solution add a solution of pure mercurous nitrate; brown, basic mercurous chromate, ($4Hg_2O{\cdot}3CrO_3$), is formed. On heating to boiling, the precipitate becomes a beautiful, fiery red, being converted into the neutral salt Hg_2CrO_4. This red salt settles very quickly, and if the precipitation is complete the solution above the precipitate will be colorless. After cooling, filter the precipitate off, wash it thoroughly with water containing a little mercurous nitrate, dry and separate from the filter as completely as possible. Burn the filter in a platinum spiral, and ignite the ash with the main portion of the precipitate, gently at first and finally strongly, in a platinum crucible under a hood with a good draft. Weigh the residue as Cr_2O_3.

* E. Schirm, *Chem. Ztg.*, **1909**, 877. Cf. p. 97. According to Schoeller and Schrauth (*ibid.*, **1909**, 1287) iron, chromium, aluminum, and zinc can be precipitated by means of aniline.

The purity of the mercurous nitrate must be tested before using it. Five grams of the salt should leave no residue after being ignited.

This excellent method for the determination of chromium unfortunately permits only a very limited application. If the solution contains any considerable amount of chloride, mercurous chloride will be precipitated with the mercurous chromate, which, although volatile on ignition, renders the precipitate too bulky and the method inaccurate.

If, therefore, it is necessary to determine chromium present as chromate in a solution containing chloride, two other methods are at our disposal. The chromate may be reduced by boiling with sulfurous acid (or by evaporating with concentrated hydrochloric acid and alcohol) and analyzed according to (*a*), or it may just as accurately, and much more conveniently, be determined by precipitating as

Barium Chromate

which is weighed after gentle ignition.

Procedure. — To the boiling neutral solution, or one weakly acid with acetic acid, add a solution of barium acetate, drop by drop,* and, after standing for some time, filter through a Gooch crucible (without using very strong suction, as otherwise the filter will soon get stopped up and the solution will filter extremely slowly). Wash the precipitate with hot water till all soluble barium salt is removed, then with dilute alcohol and dry in the hot closet. Suspend the crucible in a larger one of porcelain by means of an asbestos ring (cf. p. 37) and heat, at first gently, and finally over the full flame of a good Bunsen burner. After 5 minutes remove the cover and continue heating until the precipitate appears a uniform yellow throughout. Cool in a desiccator and weigh as $BaCrO_4$.

Sometimes the precipitate appears green on the sides of the crucible owing to a slight reduction (by means of dust, traces of alcohol, etc.) of chromic acid to chromic oxide. The latter gradually takes on oxygen from the air during the long-continued heating of the open crucible, so that the green color gradually disappears.

If a grams of chromate were taken for analysis, and the barium chromate precipitate weighed p grams, then the amount of chromium present may be calculated as follows:

$$x = \frac{100 \text{ Cr}}{\text{BaCrO}_4} \cdot \frac{p}{a} = \text{per cent Cr}$$

* If the barium acetate solution is added too quickly some of it will be carried down with the barium chromate, so that too high results will be obtained.

Example for practice: Potassium dichromate, $K_2Cr_2O_7$, purified and dried as described on pp. 49 and 50.

Weigh out about 0.5 g of the salt. Dissolve in 300 ml of water, add ammonia till neutral and then 10 drops of 6 *N* acetic acid. Heat to boiling, slowly add the barium acetate solution, and continue as described above.

Chromium originally present as chromate, or obtained as such after suitable oxidizing treatment, may be determined accurately by volumetric methods described in Part II.

Uranium, U. At. Wt. 238.2

Forms: U_3O_8 and UO_2

Determination as U_3O_8

Uranium is almost always precipitated by means of ammonia as ammonium uranate $(NH_4)_2U_2O_7$ and changed to U_3O_8 by gentle ignition in a platinum crucible with free access of air. The method is accurate if nothing else is present that will precipitate on neutralizing the solution and if care is taken to avoid the presence of CO_2; $(NH_4)_2U_2O_7$ dissolves in $(NH_4)_2CO_3$, forming $(NH_4)_4[UO_2(CO_3)_3]$. The precipitation with ammonia should be carried out as described for aluminum, and the ammonium uranate precipitate should be washed with hot 2 per cent ammonium nitrate solution.

According to the temperature of ignition, the U_3O_8 appears dirty green or black, and is difficultly soluble in dilute hydrochloric or sulfuric acids; in nitric acid it dissolves gradually. By heating with dilute sulfuric acid (1 vol. conc. H_2SO_4 + 6 vol. H_2O) in a closed tube at 150°–175° for a long time (W. F. Hillebrand),* the U_3O_8 is completely dissolved with the formation of uranous and uranyl sulfates:

$$U_3O_8 + 4\ H_2SO_4 = 2\ UO_2(SO_4) + U(SO_4)_2 + 4\ H_2O$$

U_3O_8 is also readily soluble in dilute sulfuric acid in the presence of potassium dichromate. These two last facts are taken advantage of in the volumetric determination of uranium (which see).

If the ammonium uranate precipitate is heated over a Méker burner, or blast lamp, in a stream of hydrogen, it is converted into UO_2. This method also gives accurate results.

Precipitation from a Solution containing Cupferron

Cupferron, $C_6H_5{\cdot}NO{\cdot}ONH_4$, which is the ammonium salt of phenylnitrosohydroxylamine, is a valuable reagent because it precipitates iron, vanadium, zircon-

* *Bull. U. S. Geol. Survey,* **78**, p. 90.

ium, titanium, tin, columbium, and tantalum in strongly acid solutions. Uranium in uranyl salts, in which the valence of the uranium is six, is not precipitated by cupferron so that a separation from ferric iron can be accomplished; but if, after the iron precipitate has been removed, the uranium is reduced to the quadrivalent state, all the uranium can be precipitated by means of cupferron, and the precipitate is converted into U_3O_8 by strong ignition.

Procedure. — Evaporate the filtrate from the iron determination (cf. p. 163) to about 50 ml, add 20 ml of concentrated HNO_3 and 10 ml of concentrated H_2SO_4 if not already present. Evaporate until fumes of sulfuric acid are evolved freely, cool, add 20 ml more of HNO_3, and repeat the evaporation to fumes. Continue this treatment with nitric acid until all the organic matter present is oxidized as shown by no dark color appearing on evaporating. Then, to remove the last traces of nitric acid, allow the fuming solution to cool, wash down the sides of the beaker, and again evaporate to strong fumes. Cool, dilute to make the solution contain about 6 ml of concentrated sulfuric acid per 100 ml, and pass through a Jones reductor (see Index). Rinse out the reductor with 8 per cent sulfuric acid. Cool the reduced solution to below 15°, add macerated filter paper (p. 98) and an excess of 6 per cent cupferron solution. Filter and wash with cold 4 per cent H_2SO_4 solution containing 1.5 g of cupferron per liter.

Separation of Iron, Aluminum, Chromium, Titanium, and Uranium from Calcium, Strontium, Barium, and Magnesium

To the solution containing the above substances in the presence of considerable ammonium chloride in an Erlenmeyer flask, add a slight excess of freshly prepared ammonium sulfide, free from sulfate and carbonate. After standing over night filter off the precipitate and wash it with water containing ammonium sulfide. It contains the iron and uranium as sulfides, the aluminum, chromium, and titanium as hydroxides. If large amounts of magnesium are present, some of it is almost always present in the precipitate, so that it is then necessary, after filtration, to dissolve the precipitate in hydrochloric acid and to reprecipitate with ammonium sulfide.

Instead of using ammonium sulfide, the separation can be accomplished satisfactorily with ammonia; the iron must then be in the ferric condition. Carry out the treatment as described for the precipitation of aluminum with ammonium hydroxide using methyl red as indicator.

Separation of Iron from Aluminum

(1) To a boiling solution of half-normal sodium hydroxide in a porcelain dish, add the dilute, acid solution of ferric and aluminum chlo-

rides. After the solutions are all mixed make sure that an excess of alkali hydroxide is present so that all the iron is precipitated as $Fe(OH)_3$* and all the aluminum dissolved as $NaAlO_2$. Dilute with hot water and filter. For the iron determination, dissolve the precipitate in hydrochloric acid, reprecipitate with ammonia,† ignite and weigh as Fe_2O_3 (see p. 99). Precipitate the aluminum as hydroxide in the filtrate by acidifying with nitric acid and then adding ammonia. Filter, wash with 2 per cent ammonium nitrate solution, ignite and weigh as Al_2O_3.

(2) Add three times as much tartaric acid as corresponds to the weight of dissolved Fe_2O_3 and Al_2O_3 and pass hydrogen sulfide into the solution until it is saturated. Add a very slight excess of ammonia, and allow the sulfide of iron to settle in a closed Erlenmeyer flask. Filter, wash with water containing ammonium sulfide, dissolve in hydrochloric acid, oxidize with a little potassium chlorate or nitric acid, and precipitate as ferric hydroxide by the addition of ammonia. Determine the aluminum in the filtrate by evaporating to dryness with the addition of a little sodium carbonate and potassium nitrate.‡ Gently ignite the residue in a platinum dish to destroy the tartaric acid, dissolve the residue in dilute nitric acid, filter off the carbon, and precipitate the aluminum from the solution by the addition of ammonia.

(3) Add sodium carbonate solution to the neutral solution of the chlorides or sulfates (not the nitrates) until a slight permanent precipitate is formed; dissolve this by the addition of a few drops of hydrochloric acid. Dilute the solution to about 250 ml for each 0.1 or 0.2 g of the metals present, add an excess of sodium thiosulfate solution, and boil the solution until every trace of SO_2 has disappeared. By this operation the ferric salt is reduced to ferrous salt:

$$2\,Na_2S_2O_3 + 2\,FeCl_3 = 2\,NaCl + Na_2S_4O_6 + 2\,FeCl_2$$

and the aluminum is precipitated as the hydroxide:

$$2\,AlCl_3 + 3\,H_2O + 3\,Na_2S_2O_3 = 6\,NaCl + 3\,SO_2\uparrow + 3\,S + 2\,Al(OH)_3$$

Filter off the precipitate of aluminum hydroxide and sulfur, wash with hot water, dry, transfer as completely as possible to a porcelain crucible, burn the filter in a platinum spiral and add the ash to the crucible. Ignite gently until all the sulfur has been expelled and then more

* If the precipitate is large, it should be dissolved in hydrochloric acid and again precipitated with NaOH.

† It is very hard to wash the NaOH precipitate free from alkali so that the first precipitate should not be weighed.

‡ For the direct determination of aluminum by precipitation with tannin and without destroying tartaric acid, see pp. 176, 177.

strongly over the blast, Méker or Teclu burner until the weight is constant. Cf. p. 96.

To determine the iron, make the filtrate acid with hydrochloric acid, boil off the SO_2, filter off the sulfur, oxidize the solution with nitric acid, and precipitate the iron as ferric hydroxide as described on p. 99.

Or add ammonia and ammonium sulfide to the filtrate from the $Al(OH)_3$ precipitate, filter and wash with hot water. Dissolve the iron sulfide in hot $2\,N$ hydrochloric acid, oxidize to the ferric condition with concentrated nitric acid, dilute, and precipitate with ammonia according to p. 99.

(4) Precipitate both iron and aluminum with ammonia, filter, wash, dry, ignite in a porcelain or platinum crucible, and determine the weight of the combined oxides. After a constant weight is obtained, digest the mixed oxides with concentrated hydrochloric acid to which a little water has been added (10 HCl : 1 H_2O) in a covered crucible until the iron is completely dissolved. If ferric oxide predominates, as it frequently does, the solution is effected in 1 or 2 hours. If, on the other hand, a relatively large amount of alumina is present, as is usual with silicates, a condition which can be predicted by the color of the precipitate produced by ammonia, the precipitate dissolves very slowly and many times only incompletely.

In the latter case instead of treating with hydrochloric acid, fuse the ignited oxides with 12–15 times as much potassium pyrosulfate, $K_2S_2O_7$ (cf. Vol. I).* The conversion of the oxides into sulfates is usually complete in 2–4 hours.† Place the crucible together with its cover in a beaker, add water and a little sulfuric acid, and dissolve the melt by warming gently and passing a current of air through the solution in order to keep the liquid in motion. A small amount of platinum is always dissolved by this treatment.‡ After removing the crucible and its cover, heat the solution to boiling and reduce with hydrogen sulfide as described on p. 103. After the iron is reduced, filter off the platinum sulfide, again introduce hydrogen sulfide, and continue as described on p. 104, finally titrating the reduced iron with standard potassium permanganate in 250 ml of cold acid solution. The aluminum is determined from the weight of the combined oxides after de-

* E. Deussen finds that fusion with KF·HF works better. The platinum is not attacked and the solution is effected more readily. — *Z. angew. Chem.*, **1905**, 815.

† If the precipitate produced by ammonia is well mixed with filter-paper pulp (cf. p. 98) the ignited oxides will be obtained in a condition such that the fusion with potassium pyrosulfate can be made within 10 minutes.

‡ If the fusion is made in a silica crucible, there will be no platinum to remove.

ducting the weight of Fe_2O_3 corresponding to the volume of permanganate used in the titration.

For the determination of iron in silicates the above process is most suitable (Hillebrand). The reduction of the ferric salt to ferrous salt by means of hydrogen sulfide possesses advantages over the reduction by means of zinc, for in the former case no foreign element is introduced, and furthermore zinc serves to reduce the titanium that is almost always present in rocks, and this will be again oxidized by the permanganate, so that too high an iron value will be obtained. When titanium is present, it is better to reduce with sulfurous acid as described in Part II of this book.

If all the iron is dissolved by treating the oxides with hydrochloric acid, evaporate the solution to dryness and treat the residue with a few milliliters of dilute sulfuric acid, evaporate on the water-bath as far as possible, and then heat over the free flame until fumes of sulfuric acid are evolved. After cooling, dissolve the sulfates in water and reduce the ferric sulfate to ferrous sulfate by introducing a piece of zinc, free from iron, into the crucible and covering with a watch glass. The reduction is complete in 20–30 minutes. Filter off the slight residue of platinum* with the excess of zinc, catching the filtrate in a flask already filled with carbon dioxide. Wash the residue with water that has been boiled, and titrate the solution with potassium permanganate solution.

The latter method is to be recommended for the determination of small amounts of iron in the presence of still less aluminum, as is the case in the analysis of mineral waters.

The following procedure leads to the same end, but the results are not quite so reliable:

Dilute the solution in which the iron and aluminum are to be determined to a definite volume (*e.g.*, 250 ml) and take two aliquot portions by means of a pipet (usually 100 ml).

In one portion determine the weight of the combined oxides of iron and aluminum by precipitation with ammonia and ignition of the precipitate as described on p. 95; in the other aliquot determine the iron by titration. If the solution contains hydrochloric acid, as is usual, it is best first to precipitate the iron with ammonia, filter, wash, and dissolve in dilute sulfuric acid. Reduce this solution and titrate as described above.†

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* Platinum is perceptibly attacked by long digestion with ferric chloride solution:

$$4\,FeCl_3 + Pt + 2\,HCl = H_2PtCl_6 + 4\,FeCl_2$$

The chloroplatinic acid is reduced to platinum by the action of zinc.

† It is desirable to get rid of the hydrochloric acid on account of its action upon potassium permanganate (cf. Volumetric Analysis, under Iron). In the presence of

Separation of Iron, Aluminum, and Phosphoric Acid

Although the determination of phosphoric acid has not yet been described, its determination in the presence of iron and aluminum will now be discussed because this highly important separation is necessary in the analysis of almost all minerals containing iron and aluminum as well as in the analysis of many mineral waters. Two cases are to be distinguished:

1. The solution contains only a small amount (a few centigrams or less) of iron, aluminum, and phosphoric acid.
2. The solution contains large amounts of these substances.

1. In the first case the determination of all three constituents must be undertaken in the same portion, as otherwise errors would be introduced on account of the small quantities to be determined. First treat with ammonia as described on p. 95 whereby the iron, aluminum, and phosphoric acid are precipitated.*

Ignite the precipitate in a platinum crucible and weigh:

$$Fe_2O_3 + Al_2O_3 + P_2O_5 = A$$

Fuse the oxides with six times their weight of a mixture consisting of four parts anhydrous sodium carbonate and one part pure silica. Heat the mixture over the blast lamp or Méker burner. Cool, extract the melt with water to which a little ammonium carbonate has been added, and filter. The filtrate contains all the phosphoric acid and a very little silicic acid; the residue contains all the iron and aluminum and considerable silica.

For the determination of the phosphoric acid, evaporate the filtrate to dryness with hydrochloric acid on the water-bath in order to remove the silica, moisten the residue with $6N$ hydrochloric acid, take up in a little water, filter, and precipitate the phosphoric acid in the filtrate by the addition of ammonia and "magnesia mixture," as described under Phosphoric Acid. By igniting in a porcelain crucible change the precipitate of magnesium ammonium phosphate to magnesium pyrophosphate and from its weight p calculate the amount of phosphoric anhydride, $P_2O_5 (= B)$:

$$B = \frac{P_2O_5}{Mg_2P_2O_7} \cdot p$$

hydrochloric acid, the Zimmermann-Reinhardt method of reducing with stannous chloride and titrating with permanganate is capable of giving good results. See Part II.

* The phosphoric acid is usually present in such small amounts that the iron and aluminum are more than sufficient to effect the precipitation of all the phosphoric acid, on the addition of ammonia, as phosphates of these metals.

Subtract B and A to get the combined weight of the iron and aluminum oxides and then after determining the iron by titration the aluminum can be estimated "by difference." For the determination of the iron, take the insoluble residue obtained after treating the product of the fusion with water and ammonium carbonate and digest it with hydrochloric acid in a small porcelain crucible until the iron oxide is completely dissolved. Add a little 18 N sulfuric acid, and evaporate first on the water-bath, and then over a free flame until fumes of sulfuric anhydride are evolved. After cooling, add water and digest on the water-bath for some time. Filter off the silica, reduce the solution by means of hydrogen sulfide (cf. p. 115, sub. 4), and, after removing the excess of hydrogen sulfide, titrate the iron with permanganate solution.* From the amount of permanganate used, the quantity of ferric oxide (C) can be calculated, and by deducting this from the weight of the combined oxides, the weight of the Al_2O_3 is ascertained:

$$A - (B + C) = Al_2O_3$$

2. If the solution contains large amounts of iron, aluminum, and phosphoric acid, divide it into three aliquot portions and in one determine the value of A by precipitation with ammonia; in the second determine the phosphoric acid by the molybdate method as described under Phosphoric Acid; and in the third determine the iron by titration.

Separation of Iron from Chromium

1. The chromium is oxidized in alkaline solution by means of chlorine, bromine, or sodium peroxide to a soluble chromate, and the insoluble ferric hydroxide is filtered off. If the chromium alone is desired, it is often better to fuse with sodium carbonate and peroxide as described for the Analysis of Chromite.

Procedure. — Pour the solution of the chlorides into an Erlenmeyer flask of Jena glass, provided with a ground-glass stopper and tubes by which gas may enter and leave the flask, and add sodium hydroxide solution until strongly alkaline. Heat on the water-bath and conduct chlorine gas through the liquid, or add bromine water, until it becomes distinctly yellow and the ferric hydroxide has assumed its characteristic reddish brown color. When the oxidation is accomplished by chlorine gas, 0.5 g of the mixed oxides will be completely oxidized in 15 to 20 minutes. Dilute the solution with water and filter. Carefully make the filtrate acid with acetic acid, precipitate the chromium by the addition of barium acetate, and treat the precipitate of

* Instead of reducing the iron, the ferric salt may be titrated directly with titanous chloride or iodometrically (see Volumetric Analysis).

barium chromate as described on p. 111. Dissolve the ferric hydroxide in hydrochloric acid, reprecipitate with ammonia as described on p. 99, and weigh as ferric oxide.

Remark. — If the chromate is to be determined as barium chromate, the solution must contain no sulfuric acid. If the latter is present, reduce the chromate by evaporating with hydrochloric acid and alcohol. In the solution of chromic chloride thus obtained determine the chromium as chromic oxide after precipitation with ammonia as described on p. 109.

In the case of a precipitate containing iron and chromic oxides, fuse with sodium carbonate and a little potassium chlorate. Extract the melt with water, and determine the chromium in the aqueous solution by precipitating with barium acetate as described on p. 111. Dissolve the residue from the aqueous extraction of the fusion in hydrochloric acid, precipitate with ammonia, and determine the iron as ferric oxide, according to p. 99.

If it is desired to precipitate the chromium as mercurous chromate, fuse the precipitate containing the iron and chromic oxides with sodium carbonate and potassium nitrate, extract the melt with water, neutralize the solution with nitric acid, and precipitate with mercurous nitrate solution, as described on p. 110.

2. It has been proposed to analyze the mixture of ferric and chromic oxides by strongly igniting them in a stream of hydrogen whereby the ferric oxide is reduced to metallic iron, while the chromic oxide is unchanged. The iron could then be determined by the loss of weight. This method, although theoretically very simple, seems from experiments carried out in the Zürich laboratory to be absolutely inadequate, for ferric oxide is so enveloped in chromic oxide that it is not even approximately reduced even when heated over the blast lamp.

3. Iron may be separated from chromium by precipitating the iron with ammonium sulfide from a solution containing sufficient ammonium tartrate to prevent the precipitation of the chromium. The separation is the same as was described under Aluminum, p. 114, sub. 2.

Separation of Aluminum from Chromium

If the chromium is present as chromic salt, oxidize it to chromate by means of chlorine or bromine as described on p. 118. Make acid with nitric acid, and determine the aluminum as oxide after precipitating with ammonia as described on p. 95. In the absence of sulfuric acid the chromium can be determined in the filtrate as barium chromate (cf. p. 111). If sulfuric acid is present, reduce the chromate to chromic salt by the action of concentrated hydrochloric acid and alcohol, precipitate with ammonia, and weigh as the oxide (see p. 109).

If, however, the chromium is already present as chromate, at once precipitate the aluminum, with ammonia as hydroxide, as described on p. 95.

Separation of Iron from Titanium

It is frequently necessary to determine both iron and titanium in a precipitate produced by ammonia consisting of a mixture of these two oxides alone, but it is more often necessary to determine titanium in the presence of iron, aluminum, and phosphoric acid, all of which are precipitated by ammonia in the analysis of rocks.

For the separation of titanium from iron in the absence of alumina, the following methods are suitable:

1. Ignite the precipitate produced by ammonia and weigh the mixture of oxides. Fuse it in a silica crucible with 15–20 times as much potassium pyrosulfate. Before starting the fusion, heat the pyrosulfate, or fused potassium acid sulfate, in a silica crucible until it begins to evolve fumes of sulfuric anhydride. Fuse the oxides with this dehydrated pyrosulfate until they are converted to sulfates. Use a small flame and heat so that only a slight fuming is noticed when the crucible cover is raised. As the fusion progresses the color of the melt darkens, and the melting point of the mass rises as the sulfuric anhydride escapes. When the fusion is finished, there should be no unattacked oxide visible in the melt. If the temperature is raised too quickly, sulfuric acid escapes without reacting with the oxide, and if all the pyrosulfate is converted to sulfate, the mass expands on cooling and may crack the crucible. It is a good plan to add a little pyrosulfate at the last to prevent this or to add a little concentrated sulfuric acid to the solidified melt and then heat again. If the pyrosulfate is not anhydrous, the escaping steam will carry up some of the oxides to the top of the crucible and spatter them on the cover, and these particles are likely to escape the action of the pyrosulfate.

When the fusion is finished, cool and dissolve the melt in *cold* 2.5 per cent sulfuric acid, stirring mechanically to hasten the dissolving. If necessary, filter off any undecomposed oxide. Treat this with sulfuric and hydrofluoric acids to make sure that no silica is present and again fuse with pyrosulfate.

Dilute the solution thus obtained to a definite volume, mix and take an aliquot part for the determination of iron and another aliquot for the determination of titanium. For the iron determination reduce with hydrogen sulfide as described on p. 103, and titrate the reduced solution with standard permanganate solution. For the titanium determination, treat the other aliquot with sodium carbonate until a slight, permanent precipitate is formed; dissolve this in as little sulfuric acid as possible, saturate with hydrogen sulfide in the cold, add 5 g of sodium

acetate which has been neutralized with acetic acid,* and dilute to at least 500 ml. Conduct carbon dioxide through the solution, heat to boiling, filter hot, wash with 7 per cent acetic acid containing hydrogen sulfide, ignite wet in a crucible, and weigh as TiO_2.

Remark. — If considerable iron is present, the titanic oxide thus obtained is likely to contain iron. Fuse it again with potassium pyrosulfate and repeat the precipitation exactly as before. In this way a precipitate free from iron is obtained.

2. The Chancel-Stronmayer method of precipitating titanium is also satisfactory. Neutralize the solution obtained from the pyrosulfate fusion with sodium carbonate as described above, add an excess of sodium thiosulfate, dilute to about 400–500 ml, and boil for some time. In this way metatitanic acid and sulfur are precipitated, while iron remains in solution. During the filtration, however, the finely divided sulfur passes through the filter, so that the first method is preferable. In the presence of considerable iron the metatitanic acid obtained by this method is also contaminated with iron, so that the separation must be repeated.

Separation of Aluminum from Titanium

It has been proposed to separate aluminum from titanium by taking the slightly acid solution from the pyrosulfate fusion (p. 120), diluting to a large volume, and boiling for some time on the assumption that metatitanic acid will precipitate, leaving aluminum sulfate in solution. This method, however, is useless, for alumina is precipitated with the metatitanic acid unless the solution contains enough acid to prevent this hydrolysis, in which a considerable amount of titanic acid remains in solution.

One of the best methods of separation is that of Gooch;† it consists in boiling a solution of the two elements containing considerable free acetic acid and alkali acetate; by this means all the titanium and little, if any, of the aluminum is precipitated. If, however, the amount of aluminum present is large (as is usual in rock analysis), the separation must be repeated. In no case is there danger of the precipitation of the titanium being incomplete.

In practice it is almost always necessary to separate the titanium not from aluminum alone, but from iron and aluminum, so that the method of Gooch will be described for this more general case.

Treat the solution obtained by dissolving the pyrosulfate melt in

* Cf. footnote to p. 159.

† *Chem. News*, **52**, 55 and 68.

cold, dilute acid* with three times as much tartaric acid as the weight of the oxides, saturate with hydrogen sulfide gas, and make slightly ammoniacal. By this means all the iron is precipitated as ferrous sulfide, while the aluminum and titanium remain in solution. Filter off the iron sulfide, acidify the filtrate with sulfuric acid, heat to boiling, and filter off the precipitate of sulfur and platinum sulfide (the latter from the platinum crucible in which the fusion with pyrosulfate was made). Boil the filtrate to expel the last traces of hydrogen sulfide and destroy the tartaric acid by adding $2\frac{1}{2}$ times as much potassium permanganate as there is tartaric acid present. Add sulfurous acid until the precipitated manganese dioxide is redissolved, after which add a slight excess of ammonia and 7–10 ml of glacial acetic acid for each 100 ml of solution. Boil the solution for one minute, allow the precipitate to settle, and decant the filtrate through a filter.† Finally transfer the precipitate to the filter, and wash with 7 per cent acetic acid and finally with a little hot water. Ignite the precipitate and weigh as TiO_2.

The precipitate contains manganese and aluminum, so that it must be purified. Fuse it with three times as much sodium carbonate. Leach the melt (colored green by the manganese) with cold water, leaving sodium metatitanate‡ and some alumina undissolved. Filter off the precipitate by means of a small filter, ignite this residue in a platinum crucible, and fuse again with a *little* sodium carbonate. After cooling, dissolve the contents of the crucible in 200 ml of 0.1 N sulfuric acid. Add 5 g of sodium acetate and 20 ml of glacial acetic acid. After boiling 1 minute and allowing to stand until settled, filter the precipitate, wash with 7 per cent acetic acid, then with water, dry, ignite, and weigh. This precipitate sometimes contains aluminum. Fuse it again with sodium carbonate and treat the melt with sulfuric acid, etc., exactly as described above. This time the precipitate is usually free from aluminum, but the process should be repeated until a constant weight is obtained.

This analysis does not require much time if the quantity of titanium present is so small that the precipitates filter and wash quickly.

For the determination of very small amounts of titanium, it is advisable to use the colorimetric method proposed by Weller (cf. p. 106).

The above method of Gooch is tedious and fails to take into consideration the fact that zirconium, if present, precipitates with titanium.

* See p. 120.

† Schleicher & Schüll's filter-paper No. 589 is satisfactory for this purpose.

‡ The sodium metatitanate undergoes hydrolysis and forms a precipitate containing a much higher percentage of TiO_2.

Phosphoric and vanadic acids are also likely to precipitate with titanium and zirconium but these were removed by the fusion with sodium carbonate which forms water-soluble sodium vanadate and phosphate. The titanium precipitate is also likely to contain some adsorbed alkali ions but this error is slight in rock analysis. Thorium and cerium are also precipitated to some extent, but usually these elements are present to such a slight extent that they may be neglected. For the separation of titanium from aluminum, zirconium, and thorium by means of tannin, see p. 177. To obviate the necessity of destroying the tartaric acid in the method of Gooch, W. F. Hillebrand* recommends the following procedure:

Thornton's† Method of Precipitating Titanium and Zirconium

To the filtrate from the iron sulfide precipitate, which was formed in an ammoniacal ammonium tartrate solution to prevent the precipitation of aluminum, titanium and zirconium by ammonia (cf. p. 122), add 40 ml of 18 N sulfuric acid and boil to expel the excess of hydrogen sulfide. Cool to 15°, or below, dilute to 400 ml, and add a cold 6 per cent solution of cupferron, with constant stirring (cf. p. 163). Allow the precipitate to settle and test the supernatant solution to see if the precipitation is complete; if so, a white turbidity forms instead of a yellow precipitate. Filter and wash 20 times with cold 1.2 N hydrochloric acid. Place the precipitate and filter in a crucible and dry at 110–120°. Then ignite very cautiously with a small flame placed at the base of the inclined, partly covered crucible. There is likely to be a sudden gush of smoke when the oxidation of the organic matter starts. Gradually raise the temperature until all the organic material is destroyed. Fuse the residue with sodium carbonate, extract the melt with water, filter, and wash with dilute sodium carbonate solution. Dissolve the residue in dilute sulfuric acid and repeat the precipitation with cupferron. Ignite and weigh as TiO_2 and ZrO_2. The separation of titanium and zirconium will be discussed on p. 127.

* *Analysis of Silicate and Carbonate Rocks*, p. 166 (1919).

† W. M. Thornton, *Am. J. Sci.* [4], **37**, 407 (1914); *Chem. News*, **110**, 5 (1914); *Z. anorg. Chem.*, **87**, 375 (1914); Schroeder, *Z. anorg. Chem.*, **72**, 95 (1911); Thornton and Hayden, *Am. J. Sci.* [4], **38**, 137 (1914); *Chem. News*, **110**, 153 (1914); *Z. anorg. Chem.*, **89**, 377 (1914); Lundell and Knowles, *J. Am. Chem. Soc.*, **41**, 1801 (1919).

The Determination of Titanium in Titanium-Iron Ore
Method of Barneby and Isham*

The method is based on the volatilization of the silica by hydrofluoric acid in the presence of sulfuric acid, evaporation to dryness, and fusion with sodium carbonate and a little potassium nitrate (which converts the iron and titanium to insoluble ferric oxide and sodium titanate), extraction with hot water to remove the soluble phosphates, sulfates, and aluminates, solution of the ferric oxide and sodium titanate in hydrochloric acid, extraction of ferric chloride with ether, reduction of slight traces of iron with sulfurous acid, precipitation of the titanic acid by boiling in acetic acid solution, filtration, and ignition to titanium oxide (or the titanium may be determined colorimetrically). The method is accurate except that it fails to take into consideration the probable presence of zirconium and other rare earths which will precipitate with the titanium more or less completely. The tannin method, p. 177, provides for the separation of titanium from zirconium, thorium, etc.

Procedure. — Weigh out about 0.5 g of ore into a platinum crucible, cover with a little water, and add 5 to 10 drops of concentrated sulfuric acid, and about 2 ml of hydrofluoric acid. Heat the mixture carefully until finally no more sulfuric acid fumes are evolved. Add 5–10 g of sodium carbonate and a *little* potassium nitrate† and fuse the mixture at least 30 minutes. Cool, place the crucible and cover in a beaker, add about 25 ml of hot water, and heat until the melt is disintegrated. Ferric oxide and sodium titanate are left insoluble in hot water. Remove the crucible, and dissolve any adhering particles of ferric oxide and hydrolyzed sodium titanate in hot 6 *N* hydrochloric acid; save this solution. Filter off the residue in the beaker and wash with hot water.‡ Perforate the filter and carefully wash the residue into a clean beaker with 6 *N* hydrochloric acid. (No water is to be added from this stage of the analysis until after the subsequent treatment with ether.) Transfer the hydrochloric acid washings from the platinum crucible to the beaker and heat the entire solution on the hot plate until complete solution is effected and the total volume reduced to 15 or 20 ml. Cool, add 2 ml of 12 *N* hydrochloric acid, and transfer the solution to a separatory funnel, rinsing the beaker with 6 *N* hydrochloric acid, *d.* 1.10. Add an equal volume of ether, which has been saturated with concentrated hydrochloric acid solution, to the solution

* *J. Am. Chem. Soc.*, **32**, 957 (1910).

† The potassium nitrate is added to make sure that the crucible is not injured by any sulfide or reducible metal which may be present. Too much nitrate should not be added; it will injure the crucible and also cause the melt to effervesce badly.

‡ The residue should not be washed with too much hot water; the hydrolysis of the sodium titanate may go so far that the residue will not dissolve in hydrochloric acid.

in the funnel, insert a rubber stopper in the top, invert the funnel, open the stopcock, and shake thoroughly. Close the stopcock, place the separatory funnel in an upright position, and allow to stand 10 minutes. Then drain off the aqueous layer into a second separatory funnel. Rinse the ether twice by shaking well with 5- to 10-ml portions of $6N$ hydrochloric acid, and add the washings to the aqueous solution. Repeat the treatment with ether two or three times until the last portion of ether fails to show any greenish tinge due to the presence of dissolved ferric chloride.

Rothe,* who first made use in quantitative analysis of the fact that ferric chloride dissolved in hydrochloric acid, *d.* 1.1, can be removed by shaking with ether, recommended the double separatory funnel shown in Fig. 40 on p. 173, but an ordinary 125-ml single separatory funnel can be used satisfactorily.

Carefully heat the aqueous solution containing all the titanium, in the presence of little, if any, iron and aluminum, on a water-bath containing warm water to expel the dissolved ether, add 20 ml of $18N$ sulfuric acid, and evaporate the solution until fumes of sulfuric anhydride are evolved. Dilute the cooled solution to about 100 ml and nearly neutralize with ammonia. Add 1–2 g of ammonium bisulfite and heat the solution on the hot plate for half an hour. Now add 10–15 g of ammonium acetate, with 5–10 ml of glacial acetic acid, and boil the solution for 15 minutes. Filter, wash with 7 per cent acetic acid, ignite, and weigh as TiO_2.

Determination of Titanium in Steel†

Treat 5.00 g of drillings in a 400-ml beaker with 100 ml of $6N$ hydrochloric acid and heat until all action ceases. Add 3 g of potassium chlorate dissolved in 100 ml of water to oxidize or dissolve any metallic residue. Boil the solution until tungsten, if present, is converted into yellow tungstic acid anhydride. Dilute to 200 ml and boil 5 minutes longer. Filter into a 600-ml beaker and wash the precipitate with 10 per cent hydrochloric acid until the washings are colorless.

The tungstic acid may retain traces of titanium oxide. To recover this, digest the precipitate with $4N$ ammonium hydroxide which dissolves the tungstic acid, filter, and add the residue to the main precipitate of titanium oxide.

Dilute the first filtrate to 300 ml and add successively a slight excess of ammonium hydroxide, 3 ml of concentrated hydrochloric acid, and 25 g

* *Z. anal. Chem.*, **1901**, 809.

† Method recommended by the U. S. Steel Corporation.

of sodium thiosulfate dissolved in 50 ml of water. Then, by boiling 10 minutes, all the titanium is precipitated as metatitanic acid together with traces of aluminum, chromium, and vanadium. Filter and wash the precipitate three times with hot water. Ignite it and fuse with 3 g of sodium carbonate and a little potassium nitrate; the latter serves to oxidize the chromium. Leach the product of the fusion with water and filter off the insoluble residue which will contain all the titanium.*

Continue the analysis in either of the following two ways:

(*a*) *Gravimetric Method.* Dissolve the residue on the filter in hot 6 N hydrochloric acid, nearly neutralize with ammonium hydroxide, add 10 ml of glacial acetic acid and 10 g of ammonium acetate dissolved in water, dilute to 150 ml, and boil 3 minutes. Filter and wash the precipitate with 7 per cent acetic acid, ignite, and weigh as TiO_2.

(*b*) *Colorimetric Method.* Place the filter and precipitate of sodium titanate obtained after leaching the product of the sodium carbonate fusion with water, in a beaker containing 50 cc of hot 7.5 N sulfuric acid. When the precipitate has dissolved remove the paper by filtration into a comparison tube. Add 5 ml of hydrogen peroxide and match the color produced similarly with that obtained with known quantities of titanium.

To prepare the standards, fuse 0.26 g of pure TiO_2 with 6 g of sodium carbonate. Treat the fused mass with 50 ml of water in a 250-ml beaker. Add 100 ml of 7.5 N H_2SO_4 and heat until all is dissolved. Transfer the solution to a 250-ml measuring-flask, dilute to the mark, and mix. One milliliter of the solution contains 0.62 mg of Ti.

Determination of Titanium in Ferro-Titanium†

Decompose 1.00 g of sample with 50 ml of 7.5 N sulfuric acid and evaporate the solution to fumes of sulfuric acid. When cold, add 100 ml of water and heat to dissolve the iron salts. Filter, ignite in a platinum crucible, and determine the silicon by volatilization with hydrofluoric acid (see Silicic Acid). Weigh the residue and reserve it.

Dilute the filtrate to 400 ml, neutralize with ammonium hydroxide until a faint permanent precipitate is obtained, and then add, in succession, 3 ml of 6 N hydrochloric acid, 10 ml of glacial acetic acid, and 50 ml of 20 per cent sodium thiosulfate solution. Boil 10 minutes, filter, and wash with 7 per cent acetic acid.

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* If tungsten, molybdenum, and vanadium are absent, the oxidation with chlorate can be omitted and the method considerably shortened. In this case do not oxidize the iron, and use only 10 g of thiosulfate.

† Method recommended by the U. S. Steel Corporation.

Fuse the impure TiO_2, together with the residue from the silica determination, with 5 g of sodium carbonate. Disintegrate the fused mass with water and filter off the water-soluble sodium phosphate and aluminate. Dissolve the residue on the paper in hot 6 N hydrochloric acid and precipitate in the same way as before by adding ammonia, acetic acid, and sodium thiosulfate. Filter, wash with 7 per cent acetic acid, ignite, and weigh as TiO_2.

Determination of Titanium in Iron and Steel*

Dissolve the sample (5 g) in 40 ml of hydrochloric acid (*d.* 1.10). Filter off the insoluble residue, wash with water, ignite in a platinum crucible, and treat with hydrofluoric and sulfuric acids to eliminate silica. Fuse the residue with sodium carbonate, leach the fused mass with water, filter, and dissolve the insoluble matter in sulfuric acid. Compare the amount of titanium in this solution with a standard solution by proceeding as follows: Add a sufficient amount of ferric alum to the standard titanium solution to give the same tint as the sample when they are at the same dilution. Add 2 ml of 3 per cent hydrogen peroxide to the solution and standard respectively and compare in a colorimeter.

The Separation of Zirconium from Iron, Aluminum, Chromium, Titanium, Cerium, and Thorium

Zirconium, although almost always present in small quantities in rocks, is an element seldom determined in the past by the analytical chemist. It is very similar to titanium in its properties but is much less common. Rocks rarely contain more than 0.2 per cent of this element and usually less than 0.005 per cent. Zirconium, like titanium, although to less extent, is used in steel-making, so that the steel-works chemists are now interested in the determination of zirconium in ores and in the metals and alloys derived from them.

At present the most popular method for determining zirconium† consists in precipitating secondary zirconium phosphate, $ZrH_2(PO_4)_2$, from a cold or tepid solution containing 20 per cent by weight of concentrated sulfuric acid, by means of a large excess of diammonium phosphate. In the presence of hydrogen peroxide, titanium is not precipitated. In this way zirconium can be precipitated in the presence of iron, aluminum, chromium, cerium and thorium.

Procedure. — For small quantities of zirconium (0.5 mg) the volume of the solution should be reduced to 25 ml before attempting to pre-

* Method used at the Bureau of Standards, Washington, D. C.

† Bailey, *J. Chem. Soc.*, **49**, 149, 481 (1886); Steiger, *J. Wash. Acad. Sci.*, **8**, 637 (1918); Nicolardot and Reglade, *Compt. rend.*, **168**, 348 (1919); Johnson, *Chem. Met. Eng.*, **20**, 588 (1919); Ferguson, *Eng. Mining J.*, **106**, 793 (1918); Hillebrand, *Analysis of Silicate and Carbonate Rocks*, p. 173 (1919); Lundell and Knowles, *J. Am. Chem. Soc.*, **41**, 1801 (1919) and *J. Ind. Eng. Chem.*, **12**, 562 (1920).

cipitate zirconium phosphate. With larger quantities, the volume should be increased and amount to 200 ml for the precipitation of 0.1 g of zirconium. To the neutral solution add concentrated sulfuric acid until 20 per cent by weight is present. Add sufficient hydrogen peroxide to change all the titanium to pertitanic acid and at least 10 times as much ammonium phosphate as required theoretically to form $ZrH_2(PO_4)_2$. For small quantities of zirconium an excess of 100 times the theoretical quantity is desirable. Keep the solution at 40°–50° for 2 hours, if more than 5 mg of zirconium is present, and for at least 6 hours if the quantity of zirconium is smaller. Decant as much as possible of the supernatant liquid through a filter and wash with cold 5 per cent ammonium nitrate until the excess ammonium phosphate is removed. Do not wash with pure water as it causes hydrolysis of the precipitate, leaving less phosphoric acid in proportion to the zirconium. Moreover, it is easier to get a white, ignited precipitate when the filter and precipitate contain some ammonium nitrate. Ignite very carefully in an open crucible using a low flame until all the filter paper carbon has been consumed: then raise the temperature to the full heat of a Méker burner or the blast lamp. Weigh as ZrP_2O_7.

If the weight of the precipitate exceeds a few centigrams, it is better to fuse with sodium carbonate, extract the product with hot water, and weigh the residue as ZrO_2.

Determination of Zirconium, Aluminum, and Titanium in Steel

Dissolve 5 g of steel in 50 ml of concentrated hydrochloric acid and add small portions of concentrated nitric acid until all the iron is oxidized to the ferric state. Evaporate to dryness, moisten the residue with 10 ml of concentrated hydrochloric acid, and repeat the evaporation, this time baking somewhat to remove any nitrates that may remain. Take up the residue in 50 ml of 6 N hydrochloric acid and heat until all the ferric oxide and basic salts are dissolved. Filter, wash the impure silica residue with hot, 3 per cent hydrochloric acid, and save the filtrate.

Ignite the impure silica and determine its weight if it is desired to know the silicon content of the steel. Treat with hydrofluoric acid as de cribed under Silicic Acid. Fuse the slight residue with a little potassium pyrosulfate (see p. 120). Dissolve the melt in 15 ml of 5 per cent sulfuric acid and add the solution to the acid extract obtained after the ether separation described in the next paragraph.

Evaporate the filtrate and washings from the silica determination to sirupy consistency, add 40 ml of 6 N hydrochloric acid, and extract

with ether as described on p. 124. The ether extract will contain most of the iron and molybdenum, and the acid extract will contain some iron and all of the zirconium, titanium, aluminum, manganese, chromium and copper, etc., that was present in the steel.

Evaporate the ether from the acid extract, add the sulfuric acid solution obtained from treatment of the impure silica, and heat with 0.5 ml of concentrated nitric acid to make sure that all the iron is in the ferric condition. Dilute to 200 ml and precipitate the iron, zirconium, titanium, manganese, nickel, etc., by adding 20 per cent sodium hydroxide, adding 10 ml in excess. The caustic alkali used should be pure and free from carbonate. Dissolve the precipitate in hot $6N$ hydrochloric acid, and repeat the treatment with caustic soda solution. Use the combined filtrates for the aluminum determination and this last precipitate for the determination of zirconium and titanium.

Dissolve the precipitate in hot $6N$ hydrochloric acid. Inasmuch as zirconium phosphate is not easily dissolved by acid, it is possible for some zirconium to be left on the filters used for retaining the sodium hydroxide precipitate. To recover this, ignite the filters in a platinum crucible, fuse the ash with sodium carbonate, and extract the sodium salts in the melt by treatment with hot water. Discard this aqueous solution, dissolve the residue in hot $6N$ hydrochloric acid, and add the solution to that containing the greater part of the zirconium.

Determination of Aluminum. — In the absence of chromium, uranium, and vanadium, add a few drops of methyl red indicator solution, neutralize with hydrochloric acid, and add 4 ml of concentrated acid in excess for each 100 ml of solution. Make barely alkaline with ammonia, boil 3 minutes and set aside for 10 minutes. If no precipitate forms, the absence of aluminum is assured. If a precipitate is obtained, filter it off and discard the filtrate. Without washing the precipitate, dissolve it in as little hot $6N$ hydrochloric acid as possible. Dilute to 50 ml, neutralize with ammonia, and add 2 ml of concentrated nitric acid. Heat to 50° and precipitate phosphorus with ammonium molybdate as described under the Determination of Phosphorus in Steel, by the Blair method. Filter and wash with ammonium acid sulfate solution and discard the precipitate of ammonium phosphomolybdate. Precipitate the aluminum hydroxide again with ammonium hydroxide as described above. Filter, discard the filtrate, redissolve in hot $3N$ hydrochloric acid, and reprecipitate. After washing with 2 per cent ammonium nitrate, ignite and weigh as Al_2O_3. After so much manipulation, this precipitate is certain to contain a little silica from the reagents and glassware. It should be treated with sulfuric and hydro-

fluoric acid to volatilize silicon fluoride as described under Silicic Acid, or a blank may be made carrying out every operation described above with a solution containing no iron or aluminum.

If the steel contains chromium, proceed as above until the filtrate from the ammonium phosphomolybdate precipitate is obtained. Continue as above, but before the first precipitation of the aluminum hydroxide and phosphate, add a little sodium peroxide to oxidize the chromite to chromate. Then use nitric acid instead of hydrochloric acid to neutralize the alkaline solution. The first precipitate produced by ammonia will then be free from chromium.

If the steel contains uranium, use ammonium carbonate instead of ammonium hydroxide for the final precipitation of the aluminum.

If the steel contains vanadium, the weighed Al_2O_3 will contain some vanadium. Fuse the precipitate with potassium pyrosulfate, extract the cold melt with 5 per cent sulfuric acid, and determine the vanadium content as described under Vanadium. Make a corresponding deduction from the weight of impure alumina.

Determination of Zirconium and Titanium. — Dilute the hydrochloric acid solution, obtained after dissolving the sodium hydroxide precipitate in the preceding directions, to 250 ml. Neutralize partly with ammonium hydroxide but leave about 5 per cent by volume of 6 N hydrochloric acid. Add 2 g of tartaric acid and precipitate any copper by introducing hydrogen sulfide. Filter if necessary. Add ammonia to the solution which is saturated with hydrogen sulfide and introduce more of the gas. Filter and wash with water containing 2 per cent of ammonium chloride and a little ammonium sulfide. If a precipitate forms in the filtrate, heat to boiling and filter through a new filter. The precipitate contains, besides FeS, most of the manganese and all the nickel and cobalt as sulfides. It is advisable to determine these elements in another portion of the steel.

Neutralize the ammonium sulfide filtrate with sulfuric acid, adding 30 ml of concentrated acid in excess. Digest on the steam-bath until sulfur and sulfides have coagulated. Filter, wash with 100 ml of 10 per cent sulfuric acid by volume. Cool the filtrate in ice water.

Slowly add, with stirring, an excess of a cold 6 per cent solution of cupferron (ammonium nitrosophenylhydroxylamine). The excess of the reagent is shown by the formation of a white cloud on adding the reagent and the cloud disappears instead of forming a permanent coagulated precipitate. After waiting 10 minutes, filter with gentle suction and wash thoroughly with 10 per cent hydrochloric acid. Discard the filtrate. Carefully ignite in a weighed platinum crucible and weigh the ZrO_2 and TiO_2.

Fuse the weighed oxides with potassium pyrosulfate and determine the titanium colorimetrically as described on p. 106. Deduct the corresponding weight of TiO_2 from the weight of the two oxides, or carry out the tannin separation described on p. 177.

Remarks. — Phosphorus does not interfere appreciably. Vanadium causes some trouble. If present in the steel, fuse the weighed cupferron precipitate with sodium carbonate and determine the vanadium in the water soluble extract. Fuse the insoluble residue with potassium pyrosulfate and determine the titanium colorimetrically.

Uranium may interfere slightly when present in the quadrivalent state. If this element is suspected, boil off all the hydrogen sulfide before the cupferron precipitation and oxidize the uranium to the sexivalent condition by means of permanganate and then proceed with the cupferron precipitation.

Thorium and cerium interfere but are not thrown down quantitatively with the zirconium and titanium. If these elements are suspected, proceed as follows: Take the solution after the colorimetric determination of titanium and add an excess of potassium hydroxide solution. Filter and wash once or twice by decantation and then a few times on the filter with water. Transfer to a platinum dish, add hydrofluoric acid and evaporate nearly to dryness. Take up in 5 ml of 5 per cent hydrofluoric acid (by volume). If no precipitate is visible, the rare earths are absent. If a precipitate is obtained, filter off the fluorides on a small filter resting upon a perforated platinum cone or a rubber cone. Wash the crude fluorides back into the platinum dish, add the ash of the filter and evaporate to dryness with a little sulfuric acid. Take up in hydrochloric acid and precipitate the rare earth hydroxides with ammonia. Filter, redissolve in hydrochloric acid, evaporate to dryness and treat the residue with 5 ml of boiling hot, 5 per cent oxalic acid solution. After 15 minutes, filter, wash with less than 20 ml of 5 per cent oxalic acid, ignite, and weigh. Multiply the weight obtained by 1.18 to allow for an imperfect separation of the rare earths and deduct the weight from that of the ZrO_2 obtained by the above procedure.

Separation of Beryllium (Glucinium) and Uranium

These two elements rarely occur together except in a few minerals. Neither of them is precipitated in the cold by adding an excess of ammonium carbonate to the acid solution and in this way they are different from iron and aluminum. By boiling the ammonium carbonate solution, however, basic beryllium carbonate is precipitated. If the boiling is continued long enough to make the precipitation of the beryllium quantitative, some uranium is thrown down, probably as ammonium uranate, $(NH_4)_2U_2O_7$. Hydroxylamine serves to prevent the precipitation of the latter compound by ammonium hydroxide but it does not prevent precipitation of beryllium hydroxide. Brinton and Ellestad* found it possible to develop a satisfactory method of separating beryllium and uranium by using both ammonium carbonate and hydroxylamine hydrochloride.

Procedure. — To the hydrochloric acid solution containing 0.2 g or less of beryllium and 0.3 g of uranium in a volume of about 250 ml,

* *J. Am. Chem. Soc.*, **45**, 395 (1923).

add 5 g of ammonium chloride, unless already present, and 5 g of hydroxylamine hydrochloride. Add concentrated ammonium carbonate solution until the precipitated carbonates dissolve completely in the excess of reagent. Heat to boiling and continue boiling for 30–60 seconds after the heavy white precipitate of basic beryllium carbonate forms. Filter without delay and wash thoroughly with cold water. This precipitate will contain the greater part of the beryllium and should contain no uranium.

Add hydrochloric acid in slight excess to the filtrate and heat to remove all the carbon dioxide. Add 1 g more of hydroxylamine hydrochloride and a slight excess of ammonium hydroxide after the solution has cooled. This causes the precipitation of the remainder of the beryllium as $Be(OH)_2$. Filter and wash with 2 per cent ammonium nitrate solution containing a little hydroxylamine hydrochloride. Ignite the two precipitates in a crucible, finally heating over the blast or Méker burner, and weigh as BeO.

To determine uranium, make the filtrate from the last precipitation acid with hydrochloric acid and to the cold solution add small portions of alkali bromate (keeping the beaker covered with a watch glass to prevent loss by spattering) until the solution shows the color of dissolved bromine. In this way the hydroxylamine is oxidized. Heat the solution to boiling and precipitate ammonium uranate from the hot solution by adding a slight excess of ammonium hydroxide. Wash with 2 per cent ammonium nitrate solution containing a little ammonia but no hydroxylamine hydrochloride. Ignite and weigh as U_3O_8.

Separation of Uranium from Iron and Aluminum

Treat the slightly acid solution, containing considerable quantities of ammonium salts, with an excess of ammonium carbonate and then with ammonium sulfide, allow to stand for some time in a closed flask, finally filter and wash with water containing ammonium sulfide.

The precipitate contains the iron as sulfide and the aluminum as hydroxide; in the filtrate is found all the uranium as $(NH_4)_4UO_2(CO_3)_3$. Dissolve the precipitate in hydrochloric acid. Expel hydrogen sulfide by gently boiling, oxidize the ferrous salt to ferric salt by the addition of nitric acid, and determine the iron and aluminum by one of the methods described on pp. 113–118.

Evaporate the filtrate containing the uranium almost to dryness, make acid with hydrochloric acid, boil, and precipitate the uranium as ammonium uranate by the addition of ammonia. Filter off the precipitate, wash with 2 per cent ammonium nitrate solution to which a little ammonia has been added, dry, ignite, and weigh as U_3O_8.

The result obtained may be verified by heating the residue repeatedly in a current of hydrogen in a Rose crucible (see Copper Determination) until a constant weight is obtained; weighing as UO_2. The purity of the precipitate may also be tested volumetrically (see Volumetric Analysis).

Separation of Beryllium from Aluminum

Beryllium, although a bivalent metal of Group II in the periodic classification, resembles aluminum in its reactions. Ordinarily it is determined as BeO after precipitation with NH_4OH. Because of the colloidal nature of the precipitate, the results are likely to be a little high. Moser* recommends the first two of the following methods of precipitating $Be(OH)_2$.

(*a*) To the slightly acid solution containing about 0.1 g of BeO in 100 ml, add sodium carbonate till a slight turbidity results, dissolve this in hydrochloric acid, heat to 70° and, while passing a current of air through the solution, add 50 ml of 6 per cent ammonium nitrite and 20 ml of methyl alcohol. The current of air helps to remove nitrous fumes, and the alcohol serves to form nitrous ester.

(*b*) Dilute the solution containing about 0.1 g of BeO to 300–400 ml, add 20–30 g of ammonium nitrate, and heat to boiling. Add about 1.25 g of tannin and ammonium hydroxide, drop by drop, until no further precipitation takes place. If alkali cation is present, and no other cation is permissible, dissolve the precipitate in dilute hydrochloric acid and repeat the precipitation as before.

(*c*) The following method for separating beryllium from aluminum depends on the fact that, by fusing a mixture of BeO and Al_2O_3 with sodium carbonate, the former oxide is unattacked and the latter is transformed into water-soluble sodium aluminate.†

Procedure. — Fuse the oxides for 2 to 3 hours with 5 g of sodium carbonate at a temperature slightly above the melting point of the flux. Cool, digest the melt with 300 ml of water on the steam-bath, filter, and wash the undissolved residue thoroughly with hot water. Ignite strongly and weigh as BeO. In the filtrate determine the aluminum by Blum's method (p. 95).

If the original oxides weighed only about 0.25 g, a single fusion usually suffices to accomplish a satisfactory separation; but if more is used it is advisable to fuse again with sodium carbonate and repeat the above treatment.

* Moser and Singer, *Monatsh.*, **48**, 673 (1927).

† Wunder and Wenger, *Z. anal. Chem.*, **51**, 470 (1912).

B. DIVISION OF THE PROTOXIDES

MANGANESE, NICKEL, COBALT, ZINC

MANGANESE, Mn. At. Wt. 54.93

Forms: $MnSO_4$, MnS, Mn_3O_4, $Mn_2P_2O_7$

1. Determination as Manganous Sulfate, $MnSO_4$

This method, first proposed by Volhard,* gives accurate results provided no other sulfate is present. Heating at 450–500° for an hour† is sufficient to remove all moisture and excess sulfuric acid. Long heating (17 hours) at 580° causes slight darkening, but even then the results are accurate.

Dissolve the oxide obtained by the ignition of the carbonate, sulfide, or of manganous manganite, in as little as possible of strong sulfuric acid, and some sulfurous acid if necessary to reduce Mn_3O_4, in a porcelain crucible. Evaporate as far as possible on the water-bath, remove the excess acid by heating in an electric oven, gradually raise the temperature to 450° and keep it there for 30 minutes. The heating can take place in an air-bath (Fig. 14, p. 37). When the air-bath is used, finally cover both crucibles and heat over a good Bunsen burner for 10 minutes.

(a) Precipitation of Manganese as Carbonate

This method is suitable only for the determination of manganese in solutions of pure manganese salts containing nothing else except alkali and ammonium salts.

According to H. Tamm,‡ the precipitation is best accomplished by means of ammonium carbonate. For this purpose treat the neutral solution (which may contain other ammonium salts) with a slight excess of ammonium carbonate, heat gently, and allow the beaker containing the solution to remain in a lukewarm water-bath until the precipitate has settled and the upper liquid has become clear.

Filter off the precipitate, wash with hot water, dry, ignite, and weigh either as sulfate according to 1 or as Mn_3O_4 according to 3.

* *Ann. Chem. Pharm.* **198**, 328 (1879). Cf. Marignac, *Arch. sci. phys. nat.* [3], **10**, 25 (1883); Meineke, *Chem. Ztg.*, **9**, 1478, 1787 (1885); Friedheim, *Z. anal. Chem.*, **38**, 687 (1899); Gooch and Austin, *Am. J. Sci.*, **5**, 209; Blum, *J. Am. Chem. Soc.*, **34**, 1382 (1912).

† Blum recommends a longer period of heating but in his experiments he was working with 2.4 g of manganous sulfate and considered the weight constant only when the variation was less than 0.3 mg after heating for protracted periods.

‡ *Chem. News*, **26**, 37 (1872), and *Z. anal. Chem.*, **11**, 425 (1872).

Remark. — If either sodium or potassium carbonate is used to precipitate the manganese, the precipitate will always contain alkali carbonate that cannot be removed by washing. After the precipitate has been ignited, however, the alkali carbonate can be easily extracted by water. Furthermore, the precipitation is not quite quantitative; the filtrate always contains small amounts of manganese. In order to remove this, it is necessary to evaporate the aqueous solution to dryness, whereby the manganous carbonate is completely hydrolyzed into carbonic acid and manganous hydroxide, and the latter in contact with the air changes to brown manganic oxide, Mn_2O_3. Treat the residue obtained after the evaporation with water, filter off the small amount of brown manganese compound, ignite, and add to the main part of the precipitate.

(*b*) Precipitation of Manganese as Sulfide

This method is employed when it is necessary to separate manganese from calcium, strontium, barium, and magnesium. Two cases will be discussed:

(α) The solution contains, besides manganese, considerable alkaline earths or magnesium. (β) The solution contains only small quantities of the alkaline earths or magnesium.

(α) The manganese sulfide must be precipitated in the cold in the presence of considerable ammonium salts. To the solution in an Erlenmeyer flask containing not more than 0.3 g of manganese in a volume of 200 ml, add 2 g of ammonium chloride or nitrate. If the solution reacts acid, add ammonia until it is slightly alkaline, and then a slight excess of freshly prepared, colorless ammonium sulfide solution. Fill the flask nearly full with cold distilled water that has been boiled, stopper, and allow to stand 24 hours, or longer. Then carefully decant off the clear supernatant liquid through a filter,* taking pains not to disturb the precipitate and to keep the filter filled with liquid all the time. If the precipitate is at all bulky, wash it three times by decantation with a 2 per cent solution of ammonium nitrate to which has been added 1 per cent by volume of ammonium sulfide solution. Transfer the precipitate to the filter and wash with dilute ammonium sulfide water until 20 drops of the filtrate evaporated to dryness on a crucible-cover leave no residue. Now, for the first time, allow the filter to drain completely.† Dry, transfer as much of the precipitate as possible to a small porcelain crucible, burn the filter paper in a platinum spiral, and add the ash to the main portion of the precipitate in the crucible. Heat the uncovered crucible over a small flame until the

* Schleicher & Schüll's filter-paper No. 590 can be used to advantage.

† It is often necessary to remove alkaline earth carbonate or magnesium hydroxide. To accomplish this, dissolve the precipitate in hot 2 N hydrochloric acid, evaporate to remove CO_2, and repeat the precipitation with ammonium sulfide.

greater part of the sulfur has been burned off. Treat with concentrated sulfuric acid and determine the manganese as sulfate, or ignite more strongly, finally heat over the Teclu or Méker burner, and weigh as Mn_3O_4 (cf. p. 138). Manganous sulfide is readily changed to Mn_3O_4 if the amount of sulfide is comparatively small. If more than 0.2 g is present there is danger of getting too high a result on account of some manganous sulfate not being decomposed. In this case, it is better to proceed as follows: Dissolve the washed precipitate of manganous sulfide in dilute hydrochloric acid, evaporate the solution to dryness to remove all hydrogen sulfide, dissolve the residue in a little water, transfer the solution to a weighed crucible, and determine as sulfate. Manganous sulfide can also be weighed as such. (See p. 137.)

(β) If only small amounts of alkaline earths are present, the following procedure can be used: heat the neutral solution to boiling, add an excess of ammonia and some ammonium sulfide, and continue boiling until the manganous sulfide has become a dirty green. Allow the precipitate to settle, filter, and wash with water containing a little ammonium sulfide. From this point the procedure is the same as described under (α).

(*c*) Separation of Manganese as Manganese Dioxide

If a dilute solution of a manganous salt is treated with bromine water and boiled, the reaction

$$MnCl_2 + Br_2 + 2\,H_2O \rightleftarrows MnO_2 + 2\,HCl + 2\,HBr$$

does not take place unless the halogen acids are neutralized as fast as they are formed. This neutralization can be accomplished by means of the salt of a weak acid, such as sodium acetate, even when the solution contains free acetic acid, which is very slightly ionized in the presence of its alkali salt. Thus in a solution such as is obtained after the removal of iron and aluminum by a basic acetate separation (cf. p. 158), the manganese can be precipitated quantitatively by boiling with an excess of bromine water. The oxide does not correspond exactly to MnO_2, although most of the manganese is in the quadrivalent condition.* When the precipitate has collected in large flocks, discontinue the boiling and allow the precipitate to settle; filter, and wash with hot water. Some chemists ignite this precipitate and weigh as Mn_3O_4 but it is more accurate to dissolve the precipitate in a mixture of HCl

* The MnO_2 acts as the anhydride of metamanganous acid, H_2MnO_3, and some manganous manganite, $MnMnO_3$ or Mn_2O_3, is contained in the precipitate.

and H_2SO_3 and to precipitate the manganese finally as manganese ammonium phosphate. (See 4, p. 138.)

Chlorine, hydrogen peroxide, hypochlorites, etc., may be used instead of bromine, but these reagents have no especial advantages.

If the solution of the manganous salt also contains ammonium salts the precipitation of the manganese does not take place by the above procedure, because the sodium acetate serves rather to neutralize the acid set free by the following reaction:

$$2\,NH_4Cl + 3\,Br_2 = N_2 + 2\,HCl + 6\,HBr$$

Upon the addition of ammonia, however, the precipitation of the manganese can be effected. In this case, it seems fair to assume that the reaction goes through the following stages:

$$MnCl_2 + 2\,NH_4OH \rightleftarrows Mn(OH)_2 + 2\,NH_4Cl$$

$$Mn(OH)_2 + Br_2 + 2\,NH_4OH = MnO(OH)_2 + 2\,NH_4Br + H_2O$$

The precipitation with bromine and ammonia is not so satisfactory as with bromine alone because when ammonia or ammonium salt is present much of the bromine is used up in oxidizing them. In that case there is considerable evolution of nitrogen, and, moreover, when an excess of bromine is added the solution may become acid enough to dissolve the precipitated manganese.

$$2\,NH_3 + 3\,Br_2 = 6\,HBr + N_2$$

It is necessary, therefore, when ammonium salts are present to make sure that the solution is ammoniacal at the end of the operation.

This method of precipitating manganese from solutions possesses disadvantages which make it useless in many cases. If, besides manganese, the solution contains calcium, zinc, etc., manganites of these metals are precipitated with the manganese. In this case the precipitate must be dissolved in hydrochloric acid and the precipitation repeated several times, but even then it is not possible to obtain a precipitate altogether free from these metals. If the other metals are present only in small amounts, the results obtained by this method are sufficiently accurate. The precipitation of manganese as sulfide in the presence of other metals is always satisfactory and should be used almost invariably.

2. Determination of Manganese as Sulfide

If the manganese has been precipitated, as described on p. 135, as sulfide, separate the precipitate from the filter as completely as possible, place in a Rose crucible (of unglazed porcelain), burn the filter in a platinum spiral, and add the ash to the main portion of the precipitate. Add some pure sulfur which has been crystallized from CS_2 and heat the crucible and its contents in a current of hydrogen. After the excess of sulfur has distilled off and burned, cool the crucible in the stream of hydrogen and weigh the precipitate as MnS.

3. Determination of Manganese as

Inasmuch as all the oxides of manganese, as well as those compounds which are converted into oxide on ignition (manganous salts of volatile organic and inorganic acids, with the exception of the halogen salts), are converted into Mn_3O_4* on being ignited in the air, at temperatures between 940° and 1100°, it follows that this method for the determination of manganese is quite generally applicable. It is nearly as accurate as the methods described under 1 and 2, if the ignition of the precipitate takes place in an electric furnace at about 1000°, and very good results are obtained if, as recommended by Gooch,† the porcelain crucible (containing the carbonate, manganous manganite, or sulfide) is entirely surrounded by the oxidation flame of a Teclu burner, whereby a moderately high heat is obtained without too much free access of air.

After the ignition, cool the crucible and its contents in a desiccator and weigh the Mn_3O_4.

4. Determination of Manganese as Pyrophosphate, $Mn_2P_2O_7$

This excellent method was recommended by W. Gibbs‡ and subsequently studied by Gooch and Austin.§

To the slightly acid solution, containing manganese equivalent to not more than 0.5 g $Mn_2P_2O_7$ in 250 ml, and no other metals except alkalies, add 20 g ammonium chloride, 5 to 10 ml of a cold, saturated solution of disodium phosphate (about 10 per cent), and ammonia, drop by drop, until a *slight* excess is present. Heat the solution to boiling and keep at this temperature for 3 or 4 minutes, or until the precipitate assumes a silky, crystalline appearance. After cooling, filter the precipitate into a Gooch or Munroe crucible, wash with cold ammonium nitrate solution, dry, ignite within a larger crucible or in an electric furnace. Cool in a desiccator and weigh as $Mn_2P_2O_7$.

Manganese can be determined very accurately by volumetric methods (see Volumetric Analysis).

5. Colorimetric Determination of Manganese

Small amounts of manganese can be determined accurately and quickly by the *colorimetric method*, but if more than 1.5 per cent of manganese is present the results are unreliable. The method depends

* Cf. R. J. Meyer and K. Retgers, *Z. anorg. Chem.*, **57**, 104 (1908). At 530° the oxides of manganese are slowly but quantitatively changed into Mn_2O

† *Z. anorg. Chem.*, **17**, 268 (1898).

‡ *Am. J. Science*, **46**, 216; *Z. anal. Chem.*, **7**, 101 (1868).

§ *Z. anorg. Chem.*, **18**, 339 (1898).

upon the oxidation of the manganese to permanganic acid, bringing the solution to a definite volume and comparing its color with another solution containing a known amount of manganese. If the solutions are colored exactly the same shade, then the amounts of manganese which they contain are the same. As oxidant, ammonium persulfate can be used. In hot nitric acid solutions containing silver cations, the following reaction takes place:

$$2\ Mn^{++} + 5\ S_2O_8^{--} + 8\ H_2O \rightarrow 2\ MnO_4^{-} + 10\ SO_4^{--} + 16\ H^+$$

To illustrate the method, the procedure recommended by the American Society of Testing Materials for the routine analysis of steel will be described. The method is not as reliable as the bismuthate method (see Part II). A similar procedure can be applied to the estimation of small quantities of manganese in rocks, after a solution containing all the manganese is obtained by suitable methods.*

Procedure. — Dissolve 0.1 to 0.3 g of steel in 15 ml of 25 per cent nitric acid in a small Erlenmeyer flask. Boil gently till a clear solution is obtained. Add 15 ml of 0.08 *N* silver nitrate solution, and 1 g of ammonium persulfate. Continue heating 30 seconds after the oxidation begins and bubbles of oxygen arise freely. Cool and compare the color of the solution with that obtained with a standard steel similarly treated, diluting until the colors match.

NICKEL, Ni. At. Wt. 58.69

Forms: Nickel Dimethylglyoxime, $NiC_8H_{14}N_4O_4$; Nickel, Ni; and Nickel Oxide, NiO

1. Determination as Nickel Glyoxime

Dimethylglyoxime, $CH_3{\cdot}CNOH{\cdot}CNOH{\cdot}CH_3$, was recommended by L. Tschugaeff† as a reagent for nickel and used by K. Kraut‡ for detecting the presence of traces of nickel in ashes. O. Brunck§ and others have also studied the reaction and found it to furnish a most rapid and accurate method for the quantitative estimation of nickel either by itself or in the presence of cobalt, zinc, and manganese. If the solution contains tartaric acid enough to prevent the precipitation of iron by ammonia, the nickel in a sample of nickel steel can be determined accurately within 2 hours and without the removal of any other metal.

When a dilute, neutral solution of a nickel salt is treated with an alcoholic solution of dimethylglyoxime, a red, crystalline precipitate of nickel dimethylglyoxime is formed.

$$NiCl_2 + 2\ \underset{\text{Dimethylglyoxime}}{(CH_3)_2C_2(NOH)_2} = \underset{\text{Nickel dimethylglyoxime}}{[(CH_3)_2C_2NOH{\cdot}NO]_2Ni} + 2\ HCl$$

* H. Lührig, *Chem. Ztg.*, **1914**, 781, has described a method for the determination of small quantities of manganese in water.

† *Z. anorg. Chem.*, **46**, 144 (1905); *Ber.*, **38**, 2520 (1905).

‡ *Z. angew. Chem.*, **19**, 1793 (1906); *ibid.*, **20**, 1844 (1907).

§ *Ibid.*, **20**, 834 (1907), *Stahl und Eisen*, **28**, **331**.

The salt is soluble in mineral acids so that precipitation is incomplete because of the acid set free in the reaction. It becomes quantitative, however, if the mineral acid is neutralized by ammonia or if sodium acetate is added, whereby the mineral acid is replaced by acetic acid in which the precipitate is practically insoluble. Large quantities of ammonium salts or of alkali acetate do no harm, but an excess of ammonia tends to retard the formation of the precipitate. The precipitate is distinctly soluble in absolute alcohol, but only traces dissolve in 50 per cent alcohol, and in more dilute alcohol it is even less soluble. When thrown down in the cold or in the presence of much free ammonia the precipitate is very voluminous and hard to filter.

Procedure. — Dilute the neutral or slightly acid* solution so that not more than 0.1 g of nickel is present in 200 ml, heat nearly to boiling and treat with a slight excess of an alcoholic 1 per cent solution of dimethylglyoxime.† Carefully add ammonia until the solution smells slightly of it. Allow to stand an hour if convenient, filter, while still hot, into a Gooch or Munroe crucible, wash with hot water, and dry at 110° to 120° for 45 minutes. The precipitate contains 20.31 per cent Ni.

The nickel salt of dimethylglyoxime is red and crystalline. It contains no water of crystallization and sublimes at 250° without decomposition.

2. Determination of Nickel as Metal by Electrolysis

From strongly *acid* solutions nickel is not deposited upon stationary electrodes by a current of 1–3 amperes per square decimeter of electrode surface. From slightly acid solutions the deposition is not quantitative.

From *ammoniacal* solutions nickel is easily deposited quantitatively.

(*a*) Method of Gibbs‡

Nickel sulfate or chloride (but not the nitrate) is dissolved in an ammoniacal solution of ammonium sulfate and electrolyzed.

The nickel is deposited upon a weighed cathode, and, at the end of the electrolysis, the gain in weight represents the quantity of nickel.

A suitable decomposition cell consists of a glass beaker in which is placed as cathode a wire gauze electrode (first recommended by Cl. Winkler) and as anode a platinum spiral. The electrodes must always reach to the bottom of the beaker, and the top of the gauze electrode should be nearly covered by solution. In some

* If strongly acid, neutralize the solution with sodium hydroxide.

† The volume of the alcoholic solution should not be more than half that of the nickel solution, as the precipitate is appreciably soluble in alcohol. About 0.4 g of the glyoxime should be used for each 0.1 g of nickel.

‡ *Z. anal. Chem.*, **3**, 334 (1864). Cf. Fresenius and Bergmann, *Z. anal. Chem.*, **19**, 320 (1880).

cases it is desirable to use a platinum dish as cathode, as recommended by Classen. (See Fig. 42, p. 188.)

The electrodes are usually connected with two electrode stands on which metal arms are attached to an upright glass rod (Fig. 36). To prevent serious loss of electrolyte by spattering, cover the beaker with two halves of a watch glass. This is not entirely satisfactory, as when much gas is evolved a little of the liquid is still carried off mechanically. This method of fastening the electrodes, moreover, has the disadvantage that when the electrolysis is carried out in a hot solution, acid or ammoniacal vapors, as the case may be, condense on the brass arms of the electrode support; some of the liquids thus condensed dissolve brass and the resulting solution may drop into the beaker, and spoil the analysis. To prevent this, it is better to bend the ends of the electrodes to a right angle and connect with an electrode stand designed as shown in Fig. 37.

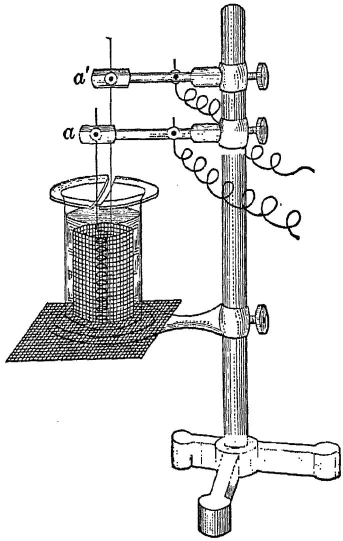

FIG. 36.

This electrode holder consists of two brass rods insulated from one another by means of an intervening layer of mica, and the rods are fastened to the ring *r* through a piece of ebonite, *e*. The openings to hold the wires are cut wedge-shaped, so that any shape of wire can be inserted.

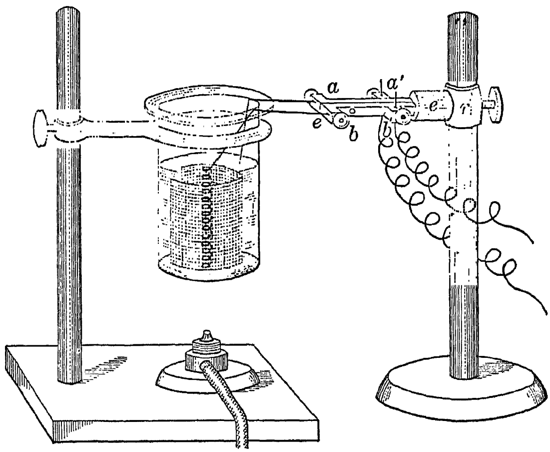

FIG. 37.

Since the ends of the electrodes leave the beaker in a horizontal direction, the beaker can be covered tightly by means of a whole watch glass, and not only are

losses by spattering avoided, but there is absolutely no danger of contamination from the outside.

Originally all electrolytic determinations were made with stationary electrodes and a weak current was passed through the solution for a long time. If too strong a current was used, very often the deposits were spongy and did not adhere well to the electrodes. This was due to the fact that hydrogen gas began to form at the cathode before the deposition of the metal was anywhere nearly complete. It

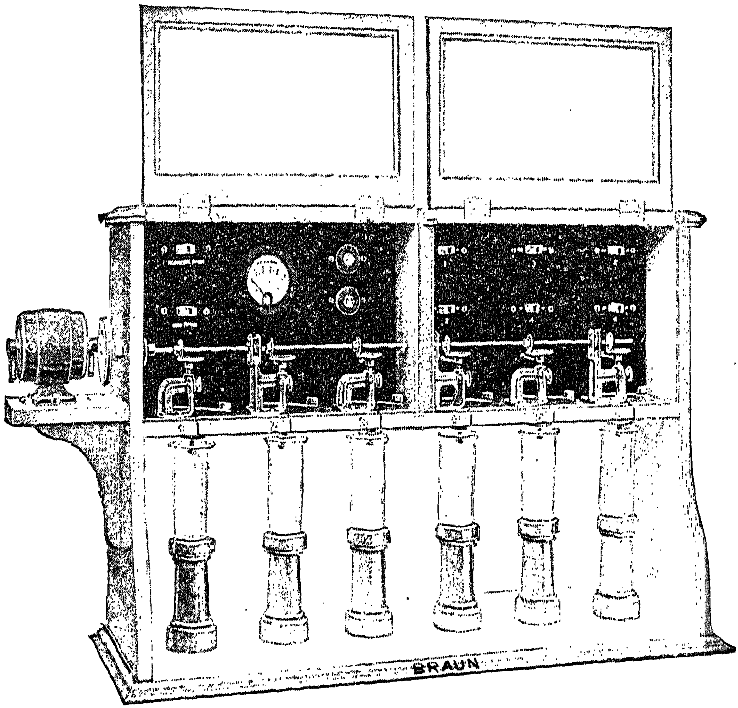

FIG. 38.

was found, however, that, by stirring the electrolyte so that the ions of the metal were kept constantly in contact with the cathode without waiting for their transference through the solution as a result of electric attraction, the current could be increased considerably and the time required shortened correspondingly. Thus by working in a concentrated solution and with a stirred electrolyte it is possible to deposit all the copper from a solution in a few minutes, whereas formerly about 20 hours would have been recommended. The Braun electrolytic apparatus (Fig. 38) has been found very satisfactory for such work with stirred electrolytes.*

* Made by the Braun Corporation of Los Angeles, California.

The Electrolysis of Ammoniacal Nickel Solution

For every 0.25–0.30 g nickel, present as sulfate or chloride but not as nitrate,* add 5–10 g of ammonium sulfate and 30–40 ml of concentrated ammonia; dilute the solution with distilled water to a volume of 150 ml. Electrolyze this solution at the room temperature with a current of 0.5–1.5 amperes and a potential difference between the electrodes of 2.8–3.3 volts. The electrolysis is finished in about 2 hours, as can be shown by adding a little water and allowing the current to pass through the solution for 15 or 20 minutes longer. If at the end of this time no nickel has deposited upon the electrode surface which was wet for the first time by the last dilution, the determination is finished. If the solution is kept at a temperature of 50°–60° C, only about 1 hour is necessary for the deposition, and the deposit adheres better to the electrode and is bright, possessing almost the color of platinum.

As soon as the electrolysis is finished, remove the watch glass, raise the electrode holder so that only the bottoms of the electrodes remain in the liquid, and wash the upper parts of the electrodes thoroughly with water from a wash-bottle. Then raise the electrodes entirely out of the solution and wash the bottoms immediately with water. Turn off the current, rinse the cathode with alcohol, and dry by holding it high above a gas flame, cool in a desiccator and weigh.

To clean the cathode, place it in a small beaker, add enough 6 N nitric acid to wet all the nickel, and heat for at least 15 minutes. This treatment is absolutely necessary to remove the last traces of nickel. If this is not done, the electrode on being ignited becomes discolored, and it is then very difficult to clean the electrode by repeated treatment with acid followed by ignition. The addition of a little copper salt to the nitric acid helps to dissolve the nickel deposit. To make sure that all the nickel has been deposited from the electrolyzed solution, nearly neutralize the ammonia with hydrochloric acid and add a few cubic centimeters of a 1 per cent solution of dimethylglyoxime in alcohol. When less than a tenth of a milligram of nickel is present, it will take several minutes for a yellow coloration to appear, and soon afterward the red crystals of nickel salt will be precipitated.

The nickel not deposited by an electrolysis may be estimated accurately by shaking the solution thoroughly and comparing the color produced by the addition of dimethylglyoxime with that produced with a dilute nickel solution containing a known quantity of nickel. Nat-

* It is possible to electrolyze ammoniacal nickel nitrate solutions but the electrolysis requires so much more time, due to the electrolytic reduction of nitrate, that it is better to remove nitric acid by evaporating the solution with sulfuric acid.

urally such a colorimetric test can be used only with very small quantities of nickel.

Remark. — The electrolysis of nickel from an ammoniacal solution should not be continued for too long a time, because the cathode slowly gains in weight even after all the nickel has been deposited from the solution. The anode is attacked, causing platinum to go into solution, which is deposited upon the cathode, partially, at least.

The presence of too little ammonia often results in the formation of black $Ni(OH)_3$ at the anode; the analysis then comes out too low. Copper, cobalt, and zinc will be deposited under the above conditions.

3. Determination as Nickelous Oxide

Heat the nickel solution in a porcelain dish with bromine water and an excess of pure potassium hydroxide; the nickel is precipitated as brownish black nickelic hydroxide, $Ni(OH)_3$. Filter off the precipitate, wash by decantation with hot water, dry, and, after burning the filter, ignite and weigh as NiO. The grayish green oxide thus obtained always contains small quantities of silicic acid and alkali,* whereby the results are too high. By treating the ignited mass with hot water, the greater part of the alkali can be removed. Drying and again igniting gives the weight of $NiO + SiO_2$. Treat the oxide in a porcelain crucible with hydrochloric acid, evaporate to dryness, moisten the dry residue with concentrated hydrochloric acid and then with hot water, filter through a small filter, wash with hot water, and ignite the filter together with the residue in a platinum crucible. The weight of this silica, SiO_2, subtracted from the former weight of $NiO + SiO_2$, gives good results.

Remark. — It is possible to precipitate nickel quantitatively as $Ni(OH)_2$ by means of caustic potash alone and the precipitate can be changed to NiO by ignition. This method is open to the same objections as the above and, furthermore, $Ni(OH)_2$ it is not so easily filtered and washed as $Ni(OH)_3$.

These two methods are more tedious to carry out and the results are not as accurate as those of the first two methods described and will probably not be used much in the future.

Besides the methods described, it has been proposed to precipitate nickel as the sulfide, and weigh it as the oxide by ignition in air.† The method is good but hardly comparable with the dimethylglyoxime method, the electrolytic method, or the volumetric titration with potassium cyanide.

* Cf. A. Windelschmidt, *Dissertation*, Münster, 1907, and W. D. Treadwell, *Dissertation*, Zurich, 1909.

† H. Cormimboef, *Ann. chim. appl.*, II, 6 (1906). Cf. A. Windelschmidt, *loc. cit.*

COBALT, Co. At. Wt. 58.94

Forms: Co, $CoSO_4$, $Co(C_{10}H_6ONO_2)_3$

1. Determination as Metal

(*a*) By Electrolysis

The most accurate method for the estimation of cobalt is by electrolysis, and the details of the process are precisely the same as have been given under Nickel, *i.e.*, from a strongly ammoniacal solution containing ammonium salts and the sulfate or chloride (preferably the former) of cobalt. It is customary to use a little more ammonia than in the determination of nickel, because cobalt has a greater tendency to deposit as black $Co(OH)_3$ at the anode. The duration of the electrolysis is the same as with nickel, rather than somewhat longer. At the end of the determination, after the electrodes have been removed, test the entire solution for cobalt by adding ammonium sulfide or potassium thiocarbonate.

(*b*) By Reduction of the Oxide in a Stream of Hydrogen

Heat the cobalt solution to boiling in a porcelain evaporating-dish, and precipitate the cobalt as black cobaltic hydroxide by the addition of caustic potash and bromine water. Filter off the precipitate,* dry, and ignite. Then cool and treat the oxides with water to remove the small quantity of alkali which is always present. Filter, ignite in a stream of hydrogen, and weigh as metal. After weighing, dissolve the metal in hydrochloric acid, evaporate the solution to dryness, moisten the dry mass with hydrochloric acid, treat with water, and filter off the small residue of silicic acid. Ignite this residue and subtract its weight from that obtained after the ignition in hydrogen. Cobalt may also be precipitated as cobaltous hydroxide by caustic potash alone, but the resulting precipitate is not so easy to filter and wash as the cobaltic hydroxide. Precipitation by means of sodium carbonate is not so satisfactory.

The oxides of cobalt when ignited in air yield a mixture of CoO and Co_3O_4 in varying proportions, so that they are not suited for the quantitative determination of cobalt.

Remark. — The results obtained by this method are usually a little higher than by electrolysis.

* Cobaltic hydroxide, unlike nickelic hydroxide, has the tendency of giving a turbid filtrate on washing. If, however, Schleicher & Schüll's filter-paper No. 589 (blue band) is used, none of the precipitate passes through.

2. Determination as Sulfate

The method is the same as was described under Manganese (p. 134).

3. Determination with α-Nitro-β-naphthol, $C_{10}H_6(NO_2)OH$

α-Nitroso-β-naphthol, $C_{10}H_6(NO)OH$, was shown in Vol. I to be a sensitive reagent for detecting small quantities of cobalt, and a procedure was given there for determining cobalt in the presence of nickel. The nitroso-β-naphthol method for separating cobalt and nickel is comparable with the potassium nitrite method which will be described later. The reagent, however, is not very stable and must be prepared freshly. Herfeld and Gerngross* and also C. Mayr† have shown that the corresponding nitro compound can be made easily from nitroso naphthol and is even more suitable for precipitating cobalt in the presence of nickel. The reagent is more stable and can be kept for a month or more; the precipitate of $Co(C_{10}H_6ONO_2)_3$ can be dried at 130° to constant weight with 9.463 per cent cobalt.

Reagent. — Dissolve 2 g of the solid in 100 ml of cold, glacial acetic acid. Add to the solution 100 ml of water, and filter.

Procedure. — To the slightly acid solution containing 1 to 30 mg of Co in a volume of 10 to 20 ml, add 10 drops of perhydrol (30 per cent H_2O_2) and enough NaOH solution to cause the formation of a slight precipitate of $Co(OH)_3$. Dissolve this precipitate in 10 ml of glacial acetic acid, dilute with hot water to 150 ml, and add 1.5 times the theoretically necessary quantity of the reagent. After a little while, filter off the precipitate into a filtering-crucible, wash three times with 30 per cent acetic acid and then with hot water, dry 45 minutes at 130°, and weigh.

This procedure serves to separate cobalt from nickel, zinc, aluminum, and chromium. In some cases a little more acid is advisable and when manganese is present, it may be necessary to add more H_2O_2 to dissolve the precipitate produced by sodium hydroxide.

ZINC, Zn. At. Wt. 65.38

Forms: $ZnNH_4PO_4$, $Zn_2P_2O_7$, ZnO, ZnS, Zn

1. Determination as Zinc Ammonium Phosphate or Zinc Pyrophosphate

This excellent method, first recommended by H. Tamm,‡ has been studied and improved by G. Lösekann and T. Meyer,§ M. Austin,|| and especially H. D. Dakin.¶

* *Z. anal. Chem.*, **94**, 8 (1933).
† *Ibid.*, **98**, 402 (1934).
‡ *Chem. News*, **24**, 148.
§ *Chem. Ztg.*, **1886**, 729.
|| *Am. J. Sci.*, **1899**; *Z. anorg. Chem.*, **22**, 212 (1900).
¶ *Z. anal. Chem.*, **39**, 273 (1900).

Procedure. — To the *cold*, acid solution of the zinc salt add ammonium hydroxide until the solution is barely acid to methyl orange. Care is necessary at this point, as zinc ammonium phosphate is soluble both in acids and ammonia. Dilute with water to a volume of 150 ml, and heat on the water-bath. To the hot solution, add 10 times as much ammonium phosphate as there is zinc present. (If the diammonium phosphate contains monammonium phosphate, the salt should be dissolved in cold water and dilute ammonia added until the solution just becomes pink with phenolphthalein.) The precipitate that first forms is amorphous but it soon changes into fine crystals of zinc ammonium phosphate. The transformation takes place more rapidly in proportion to the quantity of ammonium salts present. After the heating has continued for about 15 minutes, remove the dish from the water-bath, and after the precipitate has settled for a short time filter off the precipitate into a Gooch or Munroe crucible, wash with hot, 1 per cent ammonium phosphate solution until free from chloride etc., then twice with cold water, and finally with 50 per cent alcohol. Dry at 100–135° for an hour and weigh as $ZnNH_4PO_4$, which contains 36.64 per cent Zn. The precipitate can be washed and dried with alcohol and ether if desired (cf. p. 81).

Or the precipitate may be weighed as the pyrophosphate, $Zn_2P_2O_7$, in which case it is desirable to heat the dried zinc ammonium phosphate very slowly in an electric oven to 900–1000°. If such an oven is not at hand place the Gooch or Munroe crucible in a larger crucible and heat over the gas flame. Gradually raise the temperature until finally the full heat of the Teclu or Méker burner is reached. Heat to constant weight. $Zn_2P_2O_7$ contains 42.90 per cent Zn.

Test the filtrate from the $ZnNH_4PO_4$ precipitate with ammonia and ammonium sulfide. If a small precipitate of white zinc sulfide is formed, filter it off, using a paper filter, ignite in a porcelain crucible, and weigh as ZnO. No sulfide precipitate will be formed if the above conditions were followed carefully.

The determination as pyrophosphate is to be recommended when the zinc solution contains a very large quantity of ammonium salts because long washing is required to remove them and this renders the results a little low. When the precipitate is weighed as pyrophosphate, the ammonium salts are volatilized and it is not necessary to remove them by washing.

Remark. — In some cases, as when magnesium or aluminum is present, the procedure of K. Voigt is followed. To the solution of the zinc salt, containing ammonium salts as well, add an excess of ammonia and the required volume of ammonium phosphate solution. After standing some time, filter off the precipitated

magnesium ammonium phosphate and aluminum phosphate; the zinc ammonium phosphate is soluble in ammonia. Heat the filtrate on the water-bath until all the free ammonia has been expelled, whereby zinc ammonium phosphate separates quantitatively in the form of the crystalline precipitate. Treat this precipitate as described above. If some of the precipitate should adhere firmly to the sides of the dish, it may be dissolved in a few drops of hydrochloric acid, the solution immediately neutralized with ammonia, and heated a few minutes on the water-bath before filtering.

2. Determination as Zinc Oxide

The carbonate, nitrate, acetate, and oxalate of zinc are readily and quantitatively changed to zinc oxide by ignition in the air; in the case of the sulfate, when present in relatively large amounts, the transformation into oxide is difficult. Small amounts of the sulfate may be changed to oxide by igniting over the blast lamp. It is advisable, however, if the zinc is present as sulfate, to precipitate it from the aqueous solution as sulfide and weigh it as such according to 3; or to dissolve the sulfide on the filter in dilute hydrochloric acid, receiving the solution in a weighed platinum dish, evaporate to dryness on the water-bath, and change to oxide by the method of Volhard as described below, and weigh as such.

The chloride is readily changed to oxide, according to Volhard, by gentle ignition with pure mercuric oxide. The method is as follows: Treat the neutral solution of the chloride, contained in a platinum dish, with a large excess of pure yellow mercuric oxide,* suspended in water, and evaporate to dryness on the water-bath; mercuric chloride and zinc oxide are formed

$$ZnCl_2 + HgO = ZnO + HgCl_2$$

both of which are white substances. Enough mercuric oxide should be used so that the residue obtained after the evaporation is noticeably yellow.

Ignite the dry mass under a hood with a good draft (on account of the poisonous mercury vapors), at first gently and finally strongly, and weigh the residue of zinc oxide; both mercuric chloride and oxide are volatile. The results are excellent.

If the solution contains, besides zinc, also alkalies, the zinc can be precipitated as basic carbonate and changed to oxide upon ignition.

* The mercuric oxide is prepared by precipitating a solution of mercuric chloride with pure caustic potash. Allow the precipitate to settle, wash by decantation with water until free from chloride, and keep suspended in water in a bottle with a wide neck. A considerable amount of the mercuric oxide, say 5–10 g, should leave no weighable residue after ignition.

The precipitation of the zinc carbonate should take place in a porcelain dish and the sodium carbonate solution should be added drop by drop to the cold, barely acid solution free from ammonium salts. Add the sodium carbonate solution until the zinc solution becomes turbid, then heat to boiling; the greater part of the zinc is precipitated as granular zinc carbonate. Add 2 drops of phenolphthalein indicator solution and enough sodium carbonate solution to impart a distinct pink color. In this way a precipitate of zinc carbonate is obtained free from alkali, which is not the case if the hot solution is at once precipitated by the addition of an excess of sodium carbonate.* Filter the precipitate from the *hot* solution and wash with hot water until 20 drops of the filtrate leave no residue on evaporation. Dry the precipitate, transfer the greater part to a weighed porcelain crucible, burn the filter by itself in a platinum spiral, and add the ash to the main part of the precipitate in the crucible. Ignite at first gently and finally strongly, over a Teclu or Méker burner and weigh† after cooling in a desiccator.

If the zinc solution contains ammonium salts, it is possible to remove them by boiling with an excess of sodium carbonate solution.

3. Determination as Sulfide

This determination is chosen when the zinc is present in a solution containing ammonium salts, or when it is necessary to separate zinc from alkaline earths, alkalies, or metals of this group. Zinc sulfide may be precipitated from ammoniacal solutions, or from solutions containing free acetic, formic, citric, or thiocyanic acids in the presence of ammonium salts.

(a) *Precipitation of ZnS from Ammoniacal Solutions*

Place the slightly acid solution in an Erlenmeyer flask and treat with sodium carbonate solution until a permanent precipitate is obtained. Dissolve this by the addition of a few drops of ammonia, and then, for every 100 ml of the solution, add 5 g of ammonium acetate (or, better, ammonium thiocyanate), followed by a slight excess of freshly prepared ammonium sulfide. Nearly fill the flask with boiled water, stopper,

* If considerable amounts of ammonium salts are present there may be no precipitation. Sodium carbonate should then be added until the solution is slightly alkaline and the solution boiled until all the ammonia is expelled.

† If the solution contains sulfate, the precipitate produced by sodium carbonate always contains more or less basic zinc sulfate, which may easily lead to high results. In the presence of sulfates, therefore, it is advisable to precipitate the zinc as sulfide and determine it as such according to **3**.

and allow to stand 12 to 24 hours. Without disturbing the precipitate, pour the clear supernatant liquid through a Schleicher & Schüll's filter No. 590. Cover the precipitate with a 5 per cent solution of ammonium acetate (or ammonium thiocyanate) containing 2 ml of ammonium sulfide solution. Shake, allow to settle, and pour the turbid solution through the filter, taking care to receive the filtrate in a fresh beaker; if it comes through turbid pour it through the filter again. Repeat the decantation three times, after which transfer the precipitate to the filter and wash completely with the above wash-liquid, taking pains to keep the filter full during the entire operation, finally washing with water containing ammonium sulfide only. Dry the precipitate, transfer as completely as possible to a weighed Rose crucible, burn the filter by itself, and add the ash to the main portion of the precipitate. Mix the precipitate with one-third as much pure sulfur, cover with a layer of sulfur and heat, as described under Manganese (p. 137), in a current of hydrogen. Finally allow the crucible to cool in the stream of hydrogen and weigh the zinc sulfide.

(*b*) *Precipitation of ZnS from Acid Solutions*

To the solution, which has been nearly neutralized with ammonia, add ammonium chloride or sulfate as in the previous method and a little ammonium or sodium acetate; then saturate with hydrogen sulfide. After the precipitate has settled completely, pour the supernatant solution through a filter, and wash the precipitate with 2 to 4 per cent acetic acid which has been saturated with hydrogen sulfide. When thoroughly washed, treat as described above. It is to be noted that the zinc sulfide shows less tendency to form colloidal solutions when it is thrown down from a slightly acid solution than when it is precipitated from alkaline solutions.

The Use of Membrane Filters

Zinc sulfide is characterized by the difficulty in filtering it from solutions in which it has been precipitated. Substances of this type tend to form *colloidal solutions.* According to Wolfgang Ostwald there is no sharp dividing line between a true solution and a colloidal solution on the one hand and between a colloidal solution and a suspension on the other. Arbitrary lines may be drawn on the bases of the average size of the particles. Individual particles cannot be seen under the microscope when the diameter of the particle is less than half a wave length of light. By working with ultra-violet light of short wave length, particles about one ten-thousandth of a millimeter, or 0.1 μ,

can be seen. This value Ostwald takes to define the boundary between coarse suspensions and colloidal solutions. The pores of a good hardened filter are about 1.0 μ in diameter: those of clay and porcelain filters are about 0.2–0.4 μ. Colloidal solutions pass unchanged through paper filters and even through most of the very fine porcelain or clay filters. Suspensions do not as a rule pass through paper filters, after the pores have become clogged a little.

Typical molecules have a diameter of one ten-millionth to one millionth of a millimeter, *i.e.*, from 0.1 to 1.0 mμ. A large molecule like that of starch has a diameter of about 5 mμ.

Substances mixed with water, therefore, may be said to be in a state of molecular dispersion, or in true solution, when the diameters of the individual particles are less than 1.0 mμ and in colloidal solution when the diameters of the smallest particles lie between 1.0 mμ and 0.1 μ.

Zsigmondy* and his co-workers have developed the so-called *membrane filters* of which the pores are fine enough to separate the finer suspensions and the coarser colloids from the menstruum in which they are suspended. The filters themselves are prepared by drying a mixture of colloids. They have somewhat the appearance of parchment or of white glove leather. They can be purchased† in several grades, according to the size of the pores, and will perfectly filter colloidal solutions which will pass unchanged through an ordinary filter. Membrane filters have been recommended especially for the filtering of zinc sulfide.

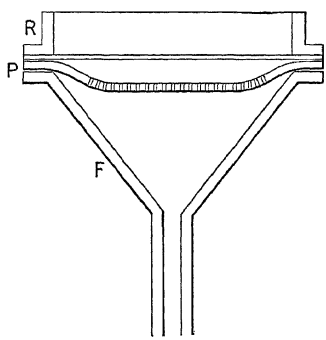

FIG. 39.

These membrane filters can be used with suction in a special filtering funnel such as that shown in Fig. 39. It consists of three parts: a funnel *F*, a perforated filter plate and a rim *R* to prevent the liquid running over. It is well to have rubber rings as gaskets between the different parts. To prepare the filter, place the filter plate, *P*, on top of the funnel, and over the perforations of the filter plate place a paper filter. If this paper is not used, only the parts of the membrane filter that lie directly over the holes in the filter plate are used in the filtra-

* Zsigmondy and Bachmann, *Z. anorg. Chem.*, **103**, 121 (1918); Zsigmondy and Jander, *Z. anal. Chem.*, **58**, 241 (1919).

† Warmbrunn, Quilitz & Co., of Berlin, Germany, and E. de Haën of Selze near Hannover, Germany, were among the first to handle Zsigmondy's filters and filtering apparatus.

tion. On top of P place a membrane filter and on this the rim, R, with rubber rings between each part. By means of three or four clamps fasten the parts in place lightly, apply suction until the membrane filter is drawn down onto the filter plate, and then tighten the clamps so that there is no chance for leakage. The whole apparatus is very similar to a porcelain Büchner funnel, except that the parts are separate.

In using these filters the liquid should not be poured up to the top of the rim and the filter should not be allowed to drain dry and form cracks.

Precipitates like silver chloride, which have to be heated and allowed to stand before filtering can be filtered immediately with a membrane filter. Precipitates of zinc sulfide which required 6 hours to filter and wash with a paper filter have been filtered and washed in 25 minutes with a membrane filter. On the other hand, time is lost if the precipitate is coarsely crystalline and filters rapidly with paper.

After filtering with a membrane filter it is usually possible to remove the precipitate completely and ignite it in a crucible by itself. The filter can be used for another filtration. Sometimes it is best to dry the precipitate before removing it and sometimes it can best be removed moist.

4. Electrolytic Determination of Zinc

It is possible to deposit zinc electrolytically with a current of 0.2–0.3 ampere from a neutral solution to which sodium acetate and a few drops of acetic acid have been added. From the solution of potassium or sodium zincate, or from the complex alkali zinc cyanides, it is easier to deposit the zinc quantitatively.

(a) Method of F. Spitzer*

To the solution of zinc sulfate (chlorides and nitrates should be absent) add a drop of phenolphthalein and sodium hydroxide solution until a permanent coloration is obtained. Then add 20–25 ml of 4 N sodium hydroxide solution, dilute to 150–200 ml, and electrolyze with a current of 0.8–1 ampere and 3–4 volts electrode potential using a platinum gauze cathode. At the end of 3 hours the electrolysis is finished, provided not more than 0.5 g of zinc was present. Without breaking the current, raise the electrodes nearly out of the bath, wash the upper portions quickly with water, then remove the electrodes entirely from the solution and rinse with water. Turn off the current, wash the cathode with alcohol, dry over a flame, cool in a desiccator, and weigh. Under these conditions, zinc forms a bluish gray deposit

* *Z. Elektrochem.*, **11**, 401 (1905).

that adheres firmly to the electrode. To make sure that all the zinc was deposited, clean the electrodes and electrolyze the solution for 30 minutes longer. A slight increase in weight will always be obtained because the anode is attacked slightly by the alkaline solution so that the cathode slowly continues to gain in weight from deposited platinum. If at the end of half an hour the gain in weight is not over 0.3 mg then the deposition of the zinc was complete the first time, as can be shown by testing with hydrogen sulfide. The results are always a little high.*

To clean the electrodes, boil them with $4N$ hydrochloric acid, wash well with distilled water, and heat over a flame. It is not necessary to cover the platinum gauze with a thin coating of copper or of silver, as has been recommended when a platinum dish is used as the cathode.

Remark. — If too little caustic soda is present, a spongy deposit of zinc is obtained which does not adhere well to the electrode. For this reason the above directions should be followed closely.

In the presence of ammonia the determination is not successful. Therefore, if it is desired to analyze a solution containing an ammonium salt, it must be boiled with caustic soda until all the ammonia has been expelled. Moreover, if chlorides or nitrates are present they must be removed by evaporation with sulfuric acid. Evaporate the solution on the water-bath and finally heat over the free flame until dense vapors of sulfuric acid are expelled. Dilute the solution and electrolyze as described.

(*b*) The Potassium Cyanide Method†

Add a drop of phenolphthalein indicator to the solution of zinc sulfate, caustic soda until a permanent pink coloration is obtained, and then potassium cyanide until a clear solution results. Dilute to a volume of 150–200 ml and electrolyze with a current of 0.2–0.3 ampere. At first the electrode potential is about 5.8 volts, but it falls during the analysis on account of the current heating the solution. The electrolysis is finished in 2 or 3 hours.

SEPARATION OF MANGANESE, NICKEL, COBALT AND ZINC FROM THE ALKALINE EARTHS

The separation depends upon the insolubility of the sulfides of the metals of this group and the solubility of the sulfides of the alkaline earths.

Procedure. — Treat the neutral solution of the chlorides in an Erlenmeyer flask with ammonium chloride (in case it is not already present)

* Ellwood B. Spear, *J. Am. Chem. Soc.*, **32**, 530 (1910). The experiments have been repeated in the author's laboratory by Janini, who obtained as an average from fourteen determinations with 50 ml of a zinc sulfate solution, the value 0.1014 g Zn instead of 0.1008 g Zn, a difference of about 0.6 per cent.

† Luckow, *Z. anal. Chem.*, **19**, 1 (1880); Beilstein and Jawein, *Ber.*, **12**, 446 (1879); Milot, *Bull. soc. chim.*, **37**, 339 (1882); W. D. Treadwell, *Electroanalyt. Methoden.*

and freshly prepared colorless ammonium sulfide solution, added drop by drop until no further precipitation takes place and the liquid has a distinct odor of ammonium sulfide. Nearly fill the flask with boiled water, stopper, and allow to stand 12 hours. Filter off the precipitate and wash as described in the Determination of Zinc (p. 150).

If only a small quantity of alkaline-earth metals is present and the ammonium sulfide solution is entirely free from ammonium carbonate, the separation is usually complete after one precipitation; in the presence of considerable calcium, strontium, barium, or magnesium the sulfide precipitate will always be more or less contaminated with these substances, so that the precipitation must be repeated. For this purpose transfer the washed precipitate as completely as possible to a porcelain crucible, burn the filter paper in a platinum spiral, and add the ash to the main part of the precipitate. Cover the crucible with a watch glass, add $2N$ hydrochloric acid, and heat gently after the evolution of hydrogen sulfide has ceased, to remove all dissolved gas. Now add a little concentrated nitric acid and heat the mixture until the precipitate is completely dissolved and the solution is evaporated to dryness, add a little concentrated hydrochloric acid, and again evaporate to make sure that no nitrate remains. Moisten the dry mass with a few drops of concentrated hydrochloric acid, dissolve in hot water, and filter off the slight residue of sulfur, which, if barium is present, always contains a small amount of barium sulfate. Wash the residue with hot water, dry, ignite in a porcelain crucible, and weigh. Treat the filtrate exactly as before with ammonium sulfide.

If nickel is present, an excess of ammonium sulfide must be carefully avoided, as otherwise some nickel sulfide will pass through the filter (cf. Vol. I). Always, however, the filtrate should be tested for nickel by acidifying with acetic acid, heating to boiling, and passing hydrogen sulfide into the solution. If a slight black precipitate is produced by this treatment, filter it off and combine with the main precipitate (cf. pp. 165 *et seq.*). Free the filtrate, containing the alkaline-earth cations, from ammonium salts by evaporating to dryness and heating the residue, dissolve this in hydrochloric acid, and examine as described on pp. 90 *et seq.*

Remark. — The ammonium sulfide solution used in the above separation must be free from ammonium carbonate. However, as all commercial ammonia contains this salt, it must be freed from carbonate before being used for the preparation of ammonium sulfide solution.

Preparation of Ammonia Free from Carbonate and Silicate

Add 10 g of freshly slaked lime to 500 ml of concentrated ammonia contained in a liter flask that is connected with a condenser. Close the condenser by means of a tube containing soda-lime, and allow the contents of the flask to stand for a day with frequent shaking. Then place 300–400 ml of water in a flask and boil, meanwhile passing through the water a current of air that has been freed from all traces of carbon dioxide by passing through concentrated caustic potash solution and then through a tower filled with soda-lime. Allow the water to cool in this air-stream. Place the flask containing the ammonia on the water-bath in such a position that the condenser tube is inclined slightly upward, and connect this with the delivery tube, through which the air previously passed into the flask of boiling water. By heating the water-bath, distil the ammonia over into the flask containing the boiled water, by which it is completely absorbed. By saturating a part of this ammonia with hydrogen sulfide, a solution of ammonium sulfide is prepared suitable for the above-described separation.

SEPARATION OF THE BIVALENT FROM THE OTHER METALS OF THE AMMONIUM SULFIDE GROUP

This separation is often designated as that of the *protoxides* from the *sesquioxides*; this designation is not applicable with titanium and uranyl derivatives.

Insoluble hydroxides or basic salts of trivalent iron, chromium, and aluminum and of quadrivalent titanium and zirconium precipitate when the acidity of the solution lies between 10^{-6} and $10^{-7.5}$ mole of hydrogen ions per liter. Bivalent uranyl ions usually precipitate also at this acidity.

It is quite common to express the acidity of a solution in terms of the so-called *hydrogen exponent*, p_H, which is the value log $1/c$ when c is the concentration of H^+ in moles per liter or exponent. Thus a concentration of 10^{-6} mole of hydrogen ions per liter is expressed briefly by saying $p_H = 6$. Since the logarithm to the base 10 of 1 is 0 and the logarithm of a fraction is the logarithm of the numerator minus the logarithm of the denominator, it is evident that $\log 1/c = 6$ when $c = 10^{-6}$.

It is easy to tell when the hydrogen-ion concentration corresponds approximately to $p_H = 5$ because methyl red indicator in dilute solution changes from red to yellow at this point. Most methods for separating ions of iron, chromium, and aluminum from the bivalent ions of the third group depend upon the neutralization of an acid solu-

tion. This may be accomplished by the careful addition of ammonia, by adding a salt of a weak acid, or by adding an insoluble carbonate or oxide. Theoretically, the separation could be accomplished by the addition of caustic alkali or alkali carbonate provided the solution was never allowed to become more alkaline than corresponds to $p_H =$ about 5, but it is practically impossible, because some portion of the solution is likely to contain a slightly lower acidity, even although it is well stirred, and the excess of this causes the precipitation of insoluble hydroxides of bivalent metals. It is difficult to make the separation with ammonium hydroxide, for this same reason, but when ammonium hydroxide is added to a solution containing an ammonium salt, its ionization is repressed so that it amounts to less than one-hundredth as much as that of a caustic alkali solution of the same normal concentration. Moreover, in ammonium hydroxide solution, the greater part of the reagent consists merely of dissolved NH_3 and this forms complex ions with many bivalent ions, particularly copper, cadmium, nickel, cobalt, and zinc ions, and the formation of these complexes prevents precipitation of hydroxides.

Chemists have known for a long time that a rough separation of the trivalent and bivalent ions can be accomplished by means of ammonia and ammonium chloride, but the practice has been discouraged because of the danger of adding too much ammonia to some part of the solution before all the solution has been sufficiently neutralized.

The Barium Carbonate Method

This method depends upon the fact that ferric, aluminum, and chromic ions (as well as titanic, zirconic and uranyl ions) are precipitated in the cold by barium carbonate, whereas the bivalent manganese, nickel, cobalt, zinc, and ferrous ions are not. Salts of the trivalent metals undergo hydrolysis when in dilute aqueous solution:

$$Fe^{+++} + HOH \rightleftarrows Fe(OH)^{++} + H^+$$

Free acid and a basic salt are formed by this hydrolysis, the composition of the salt depending upon the quantity of the water and the temperature. If the free acid is removed by the addition of barium carbonate, the equilibrium is disturbed and the hydrolysis goes further until finally the insoluble hydroxide is formed:

$$Fe(OH)^{++} + 2\ HOH \rightarrow \mathbf{Fe(OH)_3} + 2\ H^+$$

The barium carbonate, then, serves only to neutralize the acid set free by the hydrolysis, and the total reaction is expressed by the following equation:

$$2\ Fe^{+++} + 3\ HOH + 3\ BaCO_3 \rightarrow 3\ Ba^{++} + 2\ \mathbf{Fe(OH)_3} + 3\ CO_2 \uparrow$$

The salts of the bivalent metals are not subject to this hydrolysis *in the cold*, consequently they are not precipitated by the addition of barium carbonate. On warming, however, they are hydrolyzed to an appreciable extent and are then precipitated by barium carbonate.

Procedure. — Add sodium carbonate solution, drop by drop, to the slightly acid solution of the chlorides or nitrates, but not the sulfates* of the metals, in an Erlenmeyer flask until a slight, permanent turbidity is produced; redissolve this by the addition of a few drops of dilute hydrochloric acid. Dilute the solution and add pure barium carbonate† (suspended in water) until, after thoroughly shaking, an excess of the carbonate remains on the bottom of the flask. Stopper the flask and allow to stand for several hours with frequent shaking. Then decant off the clear liquid through a filter, treat the residue with cold water, and again decant. Wash the precipitate three times in this way, transfer the precipitate to the filter and wash thoroughly on the filter with cold water. The precipitate contains all the iron, aluminum, chromium, titanium, and uranium in the presence of the excess of barium carbonate. The filtrate contains the bivalent metals and barium chloride.

Dissolve the precipitate in normal hydrochloric acid solution, boil to remove carbon dioxide, and separate the iron, aluminum, chromium (titanium and uranium) from the barium‡ by double precipitation with ammonium sulfide as described on p. 153. Separate the iron, aluminum, chromium (titanium, zirconium, and uranium) from one another as described on pp. 113–133.

In the filtrate from the barium carbonate precipitation remove barium by the addition of sulfuric acid§ to the boiling solution after it has been made acid with hydrochloric acid. Filter off the barium sulfate and separate the bivalent cations from one another as described on pp. 165–171.

Remark. — The above separation of the sesquioxides from the protoxides is not absolutely certain in the presence of nickel and cobalt. In this case, particularly when considerable iron is present, the precipitate produced by barium carbonate contains a little nickel and cobalt. This difficulty can be overcome, however, by adding ammonium chloride to the solution (3–5 g for each 100 ml of solution) before precipitating with barium carbonate; the separation is then satisfactory.

* Barium carbonate will precipitate the bivalent metals when sulfates are present, *e.g.*:

$$ZnSO_4 + BaCO_3 = ZnCO_3 + BaSO_4$$

† The barium carbonate must be free from alkali carbonate.

‡ Most authorities recommend precipitating the barium first with sulfuric acid and then separating the iron, aluminum, etc. Since the precipitate of barium sulfate always contains small amounts of the heavy metals, the above procedure is preferable.

§ Or, better, by double precipitation of the other metals with ammonium sulfide.

SEPARATION OF IRON, ALUMINUM, AND TITANIUM (BUT NOT CHROMIUM AND URANIUM) FROM MANGANESE, NICKEL, COBALT, AND ZINC

Basic Acetate Method

This classic method depends upon the fact that ferric, aluminum, and titanium acetates are hydrolyzed in hot, dilute solutions much more readily than the acetates of the bivalent metals. From the equation

$$Fe(C_2H_3O_2)_3 + 2\ HOH \rightleftarrows 2\ HC_2H_3O_2 + Fe(OH)_2 \cdot C_2H_3O_2$$

it is evident that acid is set free which tends to stop the reaction, owing to the solvent action of hydrogen ions. The concentration of free hydrogen ions, however, is kept low by the addition of sodium acetate. Then, as a rule, some manganese is likely to be precipitated, so that it is advisable to dissolve the precipitate and repeat the precipitation. Hydrated manganese dioxide $MnO_2 \cdot H_2O$ or manganic hydroxide, $Mn(OH)_3$, is more insoluble than manganous hydroxide, $Mn(OH)_2$, and hence long boiling in the air tends to increase the quantity of manganese precipitated. The method is somewhat tedious, but gives excellent results.

Procedure. — To the slightly acid solution of the *chlorides*, contained in a small beaker, add sodium carbonate solution in the cold until a slight permanent opalescence is obtained; redissolve the precipitate by the addition of a few drops of dilute hydrochloric acid. Meanwhile prepare a boiling, dilute solution of sodium or ammonium acetate in a large round-bottomed flask, containing, for each 0.1–0.2 g of iron or aluminum, 1.5–2 g of acetate and 300–400 ml of water. When the iron solution is ready, take away the burner from beneath the flask, add the solution of iron, aluminum, etc., replace the burner, and continue the boiling for 1 minute. Then remove the flame (the precipitate becomes slimy on long boiling), allow the precipitate to settle, and filter while the liquid is hot through a fluted filter, washing three times by decantation with boiling water containing ammonium or sodium acetate. Spread the filter together with the precipitate upon a glass plate, rinse the bulk of the precipitate into a porcelain dish, and dissolve the precipitate remaining on the filter by alternately treating with hot 3 N hydrochloric acid and with hot water. Evaporate the resulting solution nearly to dryness on the water-bath and repeat the basic acetate precipitation exactly as before. Dissolve the filtered and washed precipitate in hydrochloric acid and separate the iron from aluminum according to p. 113. To the combined filtrates from the basic acetate precipitation, add 10–20 ml of concentrated hydrochloric acid, to prevent the precipitation of hydrated manganese dioxide, evaporate almost to dryness, dilute with a little water, and precipitate manganese, nickel, cobalt, and zinc by ammonium sulfide as described on p. 149, and analyze according to p. 165.

Remark. — This procedure requires practice. It is especially suited for the separation of iron and titanium from the protoxides; the separation is usually less satisfactory with aluminum, and so if considerable amounts of the latter are present, the barium carbonate separation is to be preferred. If it is merely a case of the

Separation of Iron from Manganese

the following modifications of the basic acetate process give satisfactory separations with only a single precipitation.

(*a*) O. Brunck's Method*

To the acid solution, containing not more than 0.3 g of iron, add 0.35 g of potassium chloride or 0.26 g ammonium chloride for each 0.1 g of iron present. Evaporate the solution to dryness on the water-bath, break up the residue by pressure with a glass rod, and heat 5 or 10 minutes longer. By this time practically all the mineral acid is expelled. Dissolve the residual salts in 10–20 ml of water, and to the resulting solution add 1.5 g of sodium acetate for each 0.1 g of iron present.† Dilute the solution with boiling water to a volume of 400–500 ml for each 0.2 g of iron present; heat, with constant stirring, until boiling begins, then remove the flame and allow the precipitate to settle. Decant off the solution through a fluted filter and wash the precipitate with hot water. Dissolve the precipitate in as little hydrochloric acid as possible, precipitate the iron by ammonia, filter, dry, and ignite as described on p. 99. Make the filtrate from the basic acetate precipitation, or better the combined filtrates from both precipitations,‡ acid with hydrochloric acid, evaporate nearly to dryness, dissolve the deposited salts in a little water, and precipitate manganese, nickel, cobalt, and zinc with ammonium sulfide according to the directions on p. 153, and separate according to p. 165.

(*b*) Method of A. Mittasch§

Neutralize the slightly acid solution, containing not more than 0.3 g of iron and having a volume of not over 100 ml, by adding ammonium carbonate solution (200 g of the commercial salt in 1 liter of water)

* *Chem. Ztg.*, **1904**, I, 513. Cf. W. Funk, *Z. anal. Chem.*, **45**, 181 (1906).

† The sodium acetate crystals sometimes contain sodium carbonate; they should be dissolved in a little water and the solution made barely acid before adding it to the iron solution.

‡ To the ammoniacal filtrate from the $Fe(OH)_3$ precipitate, add 5 ml of concentrated hydrochloric acid before adding the solution to the filtrate from the basic acetate precipitation; otherwise manganese is likely to be precipitated when the two filtrates are mixed.

§ *Z. anal. Chem.*, **42**, 508 (1903).

from a pipet or buret while stirring constantly. When a precipitate is produced which dissolves very slowly on stirring, finish the neutralization with a more dilute ammonium carbonate solution, prepared by taking 50 ml of the first solution and diluting to 1 liter. Add the dilute reagent until a slight precipitate is produced which will not dissolve by 1 or 2 minutes of stirring. At this point, add 3 ml of $2N$ acetic acid, and stir until the precipitate disappears. Dilute the solution with 400 ml of hot water and heat until it begins to boil, when the greater part of the iron will have been precipitated. Then add 20 ml of ammonium acetate solution (60 g of the commercial salt in 1 liter of water)* and continue boiling for a minute longer. Without waiting for the precipitate to settle, filter and wash with hot water until the precipitate is free from chlorides.

Dissolve the small quantity of precipitate that adheres to the sides of the vessel in which the precipitation took place by adding a few drops of hydrochloric acid, precipitate the iron in the solution by ammonia, and filter off the ferric hydroxide through a separate filter. Ignite both precipitates and filters, and weigh the iron as Fe_2O_3.

Separation of Iron and Aluminum from Manganese, Nickel, Cobalt, and Zinc

(*a*) Sodium Succinate Method

This method, applicable for the separation of large quantities of iron from small quantities of manganese, nickel, etc., is based upon the fact that ferric iron is precipitated quantitatively from *neutral* solutions as light brown ferric succinate by the addition of neutral alkali succinate solution, whereas manganese, nickel, etc., remain in solution.

Procedure. — If the solution contains free acid and all the iron is in the ferric form, neutralize with ammonia until a reddish brown coloration appears, then add sodium or ammonium acetate until the color becomes a deep brown. Dilute the solution to at least 200 ml for each 0.1 g of iron present and add 3 g of sodium succinate dissolved in a little water. Heat nearly to boiling, filter, and wash at first with cold water, then with warm normal ammonium hydroxide solution, until 20 drops of the filtrate leave no residue when evaporated to dryness on platinum. By means of the washing with ammonia, the ferric

* Commercial ammonium acetate has the symbol $NH_4C_2H_3O_2 \cdot HC_2H_3O_2$. If none of it is on hand, mix 50 ml 2 N ammonium hydroxide with 100 ml 2 N acetic acid; the mixture must be faintly acid. Of this solution use 10 ml mixed with 5 ml 2 N acetic acid for the precipitation of the iron, and use 10 ml of 2 N acetic acid to dissolve the precipitate produced by ammonium carbonate.

succinate is changed to ferric hydroxide. Ignite and weigh as ferric oxide in a porcelain crucible. If aluminum is present, analyze the ignited residue as described on p. 115. The bivalent metals in the filtrate are best precipitated by the addition of ammonium sulfide and analyzed as described on p. 165.

(*b*) Separation by Ammonia and Ammonium Chloride*

To the acid solution containing 5 g of ammonium chloride and not more than 0.2 g of iron and aluminum cations in 200 ml of solution, add a few drops of a 0.2 per cent solution of methyl red in alcohol and heat just to boiling. Carefully add normal ammonium hydroxide solution, drop by drop, until the color of the solution changes to a distinct yellow. Boil 2 minutes and filter promptly. Wash with hot 2 per cent ammonium nitrate solution until free from chloride. The precipitate contains $Fe(OH)_3$, $Al(OH)_3$, $Ti(OH)_4$ and $Zr(OH)_4$ if the corresponding elements are present.

As good a separation of iron and aluminum from manganese is accomplished in this way as by a single basic acetate precipitation. It is advisable to dissolve the precipitate and repeat the precipitation when the precipitate upon ignition is likely to weigh more than 0.1 g or when a 9-cm filter is more than half full of the precipitate.

Remark. — Lundell and Knowles showed that iron and aluminum can be separated from manganese and nickel as satisfactorily by this method of precipitation, which is the same as that recommended by Blum for precipitating aluminum, as by the basic acetate or barium carbonate methods. Phosphoric and vanadic acids follow the iron and aluminum and do not affect the separation if sufficient iron and aluminum are present. If more phosphoric acid or vanadic acid is present than is equivalent to the iron and aluminum, the separation fails as does that of the basic acetate or barium carbonate procedure. Under the above conditions, some cobalt, copper, and zinc will precipitate if present, but a fair separation is effected then by increasing the ammonium chloride content. An excess of both ammonia and ammonium chloride gives better results in the separation of iron from copper and zinc but the precipitation of the aluminum is then less complete.

The Use of Cupferron in Quantitative Analysis

Cupferron is a trivial name for the ammonium salt of nitrosophenylhydroxylamine, $C_6H_5N{\cdot}NO{\cdot}ONH_4$. O. Baudisch† first suggested its use as a reagent for the quantitative precipitation of cupric and ferric ions. By means of cupferron, it is possible to precipitate quantitatively

* Lundell and Knowles, *J. Am. Chem. Soc.*, **45**, 676 (1923).

† O. Baudisch, *Chem.-Ztg.*, **33**, 1298 (1909); Baudisch and King, *J. Ind. Eng. Chem.*, **3**, 629 (1911).

copper, iron, titanium, and zirconium from strongly acid solutions, and in this way a number of separations may be accomplished which otherwise involve considerable difficulty. The copper salt is gray, the ferric salt red, and the titanium salt yellow.

As a precipitant for copper, the reagent apparently offers no special advantages, and silver, lead, mercury, tin, or bismuth contaminates the precipitate to some extent. On the other hand, in the case of iron, titanium, and zirconium it is very useful to possess a reagent which will precipitate these elements quantitatively from acid solutions without contamination from aluminum, chromium, manganese, nickel, cobalt, zinc, or alkaline earth. The advantages of cupferron for effecting separations have been pointed out by a number of chemists.*

Cupferron is readily soluble in water, and the ammoniacal solution keeps well. The reagent is not very stable in acid solutions, particularly in hot solution or when an oxidizing agent is present. By oxidation, nitrosobenzene is formed, and its presence can be detected by the peculiar sweetish odor in nearly every precipitation with cupferron. When much nitrosobenzene is formed it separates out in the form of white needles. Precipitation with cupferron is always effected in cold, acid solution, and an excess of the reagent must be used. The precipitate is stable as long as an excess of cupferron is present.

When iron and copper are precipitated together by means of cupferron, washing with $6N$ ammonium hydroxide serves to remove the copper and the excess of cupferron; it also serves to convert the iron precipitate into ferric hydroxide, in which form it is more readily converted into ferric oxide on ignition. From the ammoniacal solution of the copper precipitate, the copper can be precipitated by the addition of acetic acid and by washing with 1 per cent sodium carbonate solution the cupferron may be removed from the copper.

Four analytical procedures illustrating the use of cupferron will be described.

1. THE DETERMINATION OF IRON IN MANGANESE ORES

Principle. — After effecting the solution of the ore, the iron is precipitated in acid solution by cupferron. The filtrate then contains all the aluminum, chromium, manganese, nickel, cobalt, zinc, and alkaline earths. After the removal of any of these elements that may be present, by washing the precipitate with cold water,

* Nissenson, *Z. angew. Chem.*, **23**, 969 (1910); Biltz and Hodtke, *Z. anorg. Chem.*, **66**, 426 (1910); Hanus and Soukup, *ibid.*, **68**, 52 (1910); R. Fresenius, *Z. anal. Chem.*, **50**, 35 (1911); Schroeder, *Z. anorg. Chem.*, **72**, 89 (1911); Bellucci and Grassi, *Gazz. chim. ital.*, **43**, I, 570; Thornton, *Am. J. Sci.*, **37**, 173 and 407 (1914); Lundell and Knowles, *J. Ind. Eng. Chem.*, **12**, 344 (1920).

the organic matter is removed and the iron converted into ferric hydroxide by washing the precipitate with ammonia. The precipitate is ignited and weighed as Fe_2O_3.

Procedure. — Dissolve about 1 g of the finely pulverized ore in concentrated hydrochloric acid, and evaporate the solution to dryness. Moisten the residue with strong hydrochloric acid, dilute with water, boil, and filter. Fuse the residue with sodium carbonate in a covered platinum crucible, and after the fusion, dissolve the melt in water and dilute hydrochloric acid. Evaporate this solution to dryness, and after the removal of the silica in the usual manner, add the filtrate to the main solution. To the cold solution add 50 ml of cupferron reagent in a fine stream down the sides of the beaker, while stirring vigorously. A brownish red, partly amorphous and partly crystalline precipitate of the ferric salt separates out. As soon as a drop of the reagent causes the formation of a snow-white precipitate of nitrosophenylhydroxylamine, all the iron is precipitated. Add a slight excess of the reagent and allow the solution to stand about 10 minutes. Filter through an ashless paper, using gentle suction. If the last particles of the precipitate cling tenaciously to the beaker, add a little ether to loosen them and remove the ether by adding a little boiling water. Wash the precipitate with cold water until the washings are no longer acid to litmus and then with 6 N ammonia to remove the excess of the reagent and form ferric hydroxide. Finally wash the filter once more with cold water. Ignite the precipitate and weigh as Fe_2O_3.

2. THE DETERMINATION OF MANGANESE IN FERROMANGANESE

Dissolve about 1 g of the material in strong hydrochloric acid and fuse the residue with sodium carbonate in a platinum crucible. Heat the melt with water and add alcohol to reduce the manganate to hydrated manganese dioxide. Filter, and dissolve the residue in hydrochloric acid; add this solution to that obtained in the first place. Precipitate iron with cupferron, as in the previous method, but do not add the ammonia washings to the solution. In the filtrate determine manganese as described on pp. 135 and 138.

3. THE DETERMINATION OF NICKEL AND COBALT IN ARSENICAL SULFIDE ORES*

Dissolve 1 g of the ore in 20 ml of a saturated solution of bromine in concentrated hydrochloric acid, and evaporate the solution somewhat to volatilize arsenious chloride. Add 10 ml of 18 N sulfuric acid and evaporate the solution until dense fumes are evolved. Dilute to 500 ml,

* H. Nissenson, *Z. angew. Chem.*, **23**, 969 (1910).

heat to boiling, and introduce hydrogen sulfide to precipitate the metals of the copper group and any remaining arsenic. In the filtrate precipitate the iron by cupferron as in Method 1, and after evaporating the filtrate until fumes of sulfuric acid are evolved, determine the nickel and cobalt according to pp. 139 and 143.

4. THE DETERMINATION OF TITANIUM AND ITS SEPARATION FROM IRON, ALUMINUM, AND PHOSPHORIC ACID*

Principle. — The iron may be reduced completely to ferrous salt by passing hydrogen sulfide into an acid solution, and then, in the presence of tartaric acid which prevents the precipitation of titanium, precipitated as ferrous sulfide in ammoniacal solution. After acidifying and boiling off the hydrogen sulfide, the titanium can be precipitated quantitatively by means of cupferron while the aluminum and phosphoric acid remain in the tartaric acid solution. It is unnecessary to remove the organic matter before igniting the yellow titanium precipitate.

Procedure. — To the solution, which should have a volume not greater than 100 ml, add at least four times as much tartaric acid as corresponds to the weight of the oxides of iron, titanium, aluminum, and phosphorus. Neutralize with ammonia, add 3 ml of 18 N sulfuric acid, and introduce hydrogen sulfide until the solution becomes colorless. Unless all the iron is reduced, the subsequent precipitate of iron sulfide will contain some titanium. After the reduction of the iron is complete, add ammonium hydroxide in considerable excess and precipitate the iron as ferrous sulfide by introducing more hydrogen sulfide gas; the solution should remain alkaline to litmus paper. Filter off the ferrous sulfide, and wash with water containing a little colorless ammonium sulfide. To the filtrate, add 40 ml of 18 N H_2SO_4 and expel the liberated hydrogen sulfide by boiling. When this is accomplished, cool the solution to room temperature, dilute to 400 ml, and treat with an excess of 6 per cent cupferron solution, added slowly down the sides of the beaker while the solution is being well stirred. After the precipitate has subsided, test the supernatant liquid by adding more of the cupferron solution. A white precipitate of nitrosophenylhydroxylamine indicates that an excess of the reagent is present, but a yellow turbidity shows that the precipitation of the titanium is incomplete. It is also well to test the filtrate in the same way. Collect the titanium precipitate on filter paper, using gentle suction, and wash 20 times with normal hydrochloric acid solution. Ignite very cautiously in a platinum or quartz crucible until the organic matter is all consumed. Finally, heat to constant weight over a Méker burner and weigh as TiO_2.

* W. M. Thornton, Jr., *Am. J. Science*, **37**, 407 (1914).

Other Determinations with Cupferron

Zirconium can be precipitated quantitatively from solutions containing as much as 40 per cent of concentrated sulfuric acid by volume, and the presence of tartaric acid has no effect upon the precipitation. The ignited precipitate is ZrO_2. Thorium, on the other hand, is not precipitated quantitatively in the presence of sulfuric acid but can be thrown down from acetic acid solutions. Vanadium, in either the quadrivalent or quinquevalent condition, can be determined quantitatively by precipitation in 1 per cent hydrochloric or sulfuric acid solution provided the precipitate is washed with 1 per cent acid containing cupferron. Tantalum and columbium are also precipitated.

Lead, silver, mercury, tin, bismuth, cerium, tungsten, interfere more or less with cupferron determinations and are likely to precipitate to some extent in most of the methods that have been described.

SEPARATION OF THE BIVALENT METALS OF THE AMMONIUM SULFIDE GROUP FROM ONE ANOTHER

Separation of Zinc from Nickel, Cobalt, and Manganese

Most methods for this separation depend upon the slight solubility of zinc sulfide and the greater solubility of the other sulfides* in their state of formation.

It was shown in Vol. I that the solubility products of ZnS, NiS, CoS, FeS, Fe_2S_3, and MnS are all so small that these substances are precipitated quantitatively whenever the corresponding cations come in contact with any appreciable concentration of sulfide ions, as by adding a solution of ammonium sulfide. It was also shown in Vol. I that hydrogen sulfide is a weak acid and only slightly ionized. By adding acid, the concentration of the sulfide ion diminishes in proportion to the square of the concentration of hydrogen ions. Thus, if to an aqueous solution of hydrogen sulfide, enough acid is added to increase the hydrogen ion concentration tenfold, the concentration of the sulfide ion is diminished to about one one-hundredth of its former value.

In a liter of water saturated with hydrogen sulfide at 25°, there is present about 0.1 mole of undissociated hydrogen sulfide, 0.9×10^{-4} mole of hydrogen ion, and only 1.2×10^{-15} mole of sulfide ion. In the saturated solution the relation $[H^+]^2 \times [S^{--}] = 1.1 \times 10^{-23}$ always holds at 25°, according to theory, and, therefore, it is easy to fix the concentration of the sulfide ion by regulating the concentration of the hydrogen ion.

* Nickel and cobalt sulfides when once formed are insoluble in dilute acids. These substances probably exist in two allotropic modifications, of which one is soluble and the other insoluble. The soluble form has never been isolated.

Thus, to take a concrete case, suppose a solution to contain 0.2 g of zinc ions and 0.2 g of ferrous ions in 400 ml of solution. What concentration of hydrogen ions is necessary to effect a quantitative separation of zinc and iron by hydrogen sulfide? Let us assume that the separation can be called quantitative when all but about 0.5 mg of zinc is precipitated and not over 0.5 mg of iron.

The solubility product of zinc sulfide is given in Vol. I as 1.2×10^{-23} and that of ferrous sulfide as 1.5×10^{-19}. Now 0.5 mg of Zn in 400 ml $= \frac{0.0005}{65.4} \times \frac{1000}{400} =$ 1.9×10^{-5} mole per liter. To reach the solubility product of ZnS it is necessary to have $\frac{1.2 \times 10^{-23}}{1.9 \times 10^{-5}} = 6.3 \times 10^{-19}$ mole per liter of S^{--} ions.

The ionization of hydrogen sulfide in a saturated solution is repressed to this value when $[H^+]^2 = \frac{1.1 \times 10^{-23}}{6.3 \times 10^{-19}} = 0.17 \times 10^{-4}$ and $[H^+] = 4 \times 10^{-3}$ mole per liter. A similar computation for FeS shows that the concentration of H^+ ions required to prevent the precipitation of 0.2 g of Fe is about 8×10^{-4} mole per liter. Therefore, to separate 0.2 g of Fe completely from 0.2 g of Zn in 400 ml of solution it is necessary to keep the concentration of the acid between 8×10^{-4} and 4×10^{-3} mole per liter or, in other words, the solution must be kept between 0.0008 and 0.004 normal in hydrogen ions.

The values for the solubility products given in Vol. I are not accurate enough to predict with certainty whether a definite separation will be accomplished satisfactorily but they indicate the possibility of such separations. The above computation, therefore, suggests the possibility of separating zinc from iron by means of hydrogen sulfide, and it has been found possible to accomplish this in the laboratory.

To reach the desired concentration of hydrogen ions it is not permissible merely to add just the right quantity of a mineral acid at the start. During the precipitation of ZnS more hydrogen ions are formed as the following equation shows:

$$Zn^{++} + H_2S = ZnS + 2\,H^+$$

It is necessary, therefore, to make sure that the acidity is correct when all the zinc is precipitated. This is more important than the acid concentration at the start, for when hydrogen sulfide is passed into a solution, the least soluble sulfide forms first; and if at one part of the solution a more soluble sulfide forms, it will itself precipitate another less soluble sulfide when it meets the other ion in another part of the solution.

Experimentally, it has been found possible to separate zinc as sulfide from very dilute hydrochloric acid solution after the addition of alkali acetate, and also from a solution containing dilute hydrochloric acid and a large quantity of ammonium salt. In the latter case it is probable that the ammonium salt exerts a "salting-out effect" and precipitates colloidal zinc sulfide, making the solubility product smaller than it apparently is in pure water.

Method of Smith and Brunner*

Procedure. — Treat the hydrochloric acid solution of the four metals with sodium carbonate until a permanent precipitate is formed, and redissolve by the addition of a few drops of $2N$ hydrochloric acid. Into this nearly neutral solution introduce hydrogen sulfide for 5 minutes, then add a few drops of $2N$ sodium or ammonium acetate solution and saturate with hydrogen sulfide. Allow the mixture to stand over night, filter, and wash with hydrogen sulfide water containing 2 per cent of ammonium salt (either the chloride, sulfate, or thiocyanate). Determine the zinc either as oxide or sulfide according to the methods described on pp. 146–149.

Remark. — Inasmuch as the exact amount of acid to be set free is unknown, it is impossible to tell exactly how much alkali acetate is necessary, and herein lies the chief difficulty. If too much alkali acetate is added, some nickel or cobalt sulfide may be precipitated (shown by the gray color of the zinc precipitate). If not enough alkali acetate is added, the zinc will not be completely precipitated. The following separation is more certain.

Method of Cl. Zimmermann†

Procedure. — Treat the slightly acid solution with sodium carbonate solution until a permanent precipitate is formed and redissolve by the addition of a few drops of $2N$ hydrochloric acid; then for every 80 ml of the solution add 10, or at the most 15, drops of $2N$ hydrochloric acid‡ and 10 ml of 20 per cent ammonium thiocyanate solution. Now heat the solution to about 70° C and saturate with hydrogen sulfide. At first the solution becomes only slightly turbid,§ but after some time pure white zinc sulfide is thrown down in clouds, constantly becoming denser. After the solution has become saturated with hydrogen sulfide, cover the beaker and allow it to stand in a warm place until the precipitate has settled and the upper liquid is clear. Then filter

* *Chem. Centrabl.*, **1895**, 26.

† *Ann. chem. pharm.*, **199**, p. 3 (1879); **204** (1880), p. 226.

‡ The addition of hydrochloric acid is in all cases necessary, because otherwise nickel sulfide will be precipitated with the zinc sulfide, especially when considerable nickel and little zinc are present.

§ There are at the start but few zinc ions in the solution. The four metals are present for the most part in the form of complex thiocyanates of the general formula $[R(CNS)_4](NH_4)_2$. The zinc salt, like carnallite (see Vol. I), is slightly dissociated,

$$[Zn(CNS)_4](NH_4)_2 \rightleftarrows Zn(CNS)_2 + 2\ NH_4CNS$$

and the zinc thiocyanate is converted into insoluble sulfide by the action of hydrogen sulfide. When the zinc begins to precipitate as sulfide, the equilibrium is disturbed and eventually all the zinc becomes precipitated.

and wash the precipitate, as described in the method of Smith and Brunner.

From the filtrate nickel, cobalt, and manganese are precipitated by means of ammonium sulfide, filtered and separated according to the following methods.

"Salting-out Method"

Experiments were performed by G. H. Kramers to determine whether the separation of zinc from nickel and cobalt could be accomplished in weakly acid solutions by hydrogen sulfide after the addition of *any* ammonium salt of a strong acid. The results obtained showed this to be possible.

Procedure. — To the neutral solution* containing nickel and zinc as sulfate or chloride (the sum of the oxides present amounting to about $\frac{1}{4}$ per cent of the weight of the solution) add 8–10 drops of $2N$ hydrochloric acid and about 2 per cent of ammonium sulfate (referred to the total amount of liquid). Saturate the solution at 50° C with hydrogen sulfide. Allow the warm solution to stand until the white precipitate of zinc sulfide has settled out, and then treat exactly as described under the Method of Zimmermann.

Separation of Manganese from Nickel and Cobalt

Treat the solution of the chlorides or sulfates with an excess of sodium carbonate, add a liberal excess of acetic acid, and, for each gram of nickel or cobalt present, introduce 5 g of ammonium acetate. Dilute the solution to 100–200 ml, heat to 70–80° C, saturate with hydrogen sulfide, filter, and wash with hot water. The manganese is in the filtrate, and the nickel and cobalt are in the precipitate.

Remark. — The filtrate often contains small amounts of nickel and cobalt. In order to remove these metals, the solution should be evaporated and colorless ammonium sulfide added. Then make slightly acid with acetic acid, warm, and filter. In case a precipitate of nickel or cobalt sulfides is formed by this treatment, test the filtrate in the same way again and repeat the process until no further precipitation is produced.

Separation of Cobalt from Nickel

(*a*) Method of Tschugaeff-Brunck†

This method is probably the quickest and most accurate for the estimation of nickel in the presence of cobalt. It depends upon the fact that nickel is quantitatively precipitated, by means of dimethylglyoxime, from a barely ammoniacal solution or from a slightly acid solution containing sodium acetate. Cobalt, under these conditions, is not precipitated.

* If the solution is acid, neutralize with sodium carbonate as described in the preceding methods.

† O. Brunck, *Z. angew. Chem.*, **1907**, 1848.

Procedure. — If the quantity of cobalt present does not exceed the quantity of nickel, the procedure is exactly the same as when nickel alone is present; with larger quantities of cobalt add two or three times as much of the dimethylglyoxime reagent and carry out the precipitation exactly as described on p. 139. For the determination of both nickel and cobalt, divide the original solution into two portions. In one portion determine the nickel as outlined above, and in the other deposit the two elements electrolytically as described on p. 140 and p. 143, and find the cobalt by difference. If only a little of the substance is available, deposit the two metals together by electrolysis, dissolve the weighed deposit in nitric acid (the electrodes must be completely immersed in the acid and the solution boiled for at least 20 minutes), concentrate the resulting solution to a small volume, and determine the nickel as described above. The method can be recommended strongly. Sometimes, when the quantity of cobalt is larger than that of the nickel, it is better to dissolve the first precipitate in nitric acid and repeat the precipitation to get a purer precipitate.

(*b*) The Potassium Nitrite Method of N. W. Fischer*

Brunck's Modification†

Evaporate the solution containing an excess of acid to dryness in a porcelain dish and treat the residue with 1 or 2 drops of $2N$ hydrochloric acid and 5–10 ml of water. Add pure caustic potash solution, drop by drop, until the reaction is barely alkaline. Dissolve the resulting precipitate in as little glacial acetic acid as possible, add half of the solution's volume of 50 per cent potassium nitrite solution and 10 drops more of acetic acid. Stir the mixture well and allow it to stand 24 hours. At the end of this time the precipitation is almost always complete. This should be proved, however, by removing a little of the undiluted solution with a pipet, adding to it a little more potassium nitrite solution, and allowing to stand a little longer. If at the end of an hour no further precipitation results, then all the cobalt has been precipitated. If a precipitate is formed, add more potassium nitrite to the main solution and again allow to stand. Decant off the clear liquid through a filter, transfer the residue to the filter, and wash with a 10 per cent potassium acetate solution until 1 ml of the filtrate on being acidified with acetic acid and boiled with 1 ml of a 1 per cent solution of dimethylglyoxime will show no test for nickel. This is usually the case after washing four times. Transfer as much of the

* *Pogg. Ann.*, **71**, 545 (1847).

† *Z. angew. Chem.*, **1907**, 1847.

precipitate as possible to a small porcelain dish, cover with a watch glass, cautiously acidify with sulfuric acid, and heat on the water-bath until no more brown vapors are evolved. Dissolve the small quantity of precipitate remaining on the filter by pouring hot, dilute sulfuric acid through the filter and add this acid to the main solution of the cobalt. After evaporating as far as possible on the water-bath, continue heating on an air-bath until dense vapors of sulfuric acid are evolved. After cooling, dissolve the residue in water and determine the cobalt electrolytically, as described on p. 145. If it is not convenient to carry out an electrolysis, dissolve the nitrite precipitate in hydrochloric acid and determine the cobalt according to p. 145 (*b*).

Remark. — This method gives reliable results provided the solution is free from alkaline earths. If not, the nickel and alkaline-earth metals are precipitated with the cobalt. (Cf. Vol. I.)

(*c*) Method of Ilinsky and von Knorre*

This method depends upon the fact that cobalt can be precipitated as purple-red $[C_{10}H_6O(NO)]_3Co$ by treatment with α-nitroso-β-naphthol in hydrochloric acid solution. Nickel is not precipitated under these conditions.

Procedure. — To the neutral solution containing not more than 0.2 g of nickel and 0.1 g of cobalt, add 10 ml of 6 N hydrochloric acid, dilute to 200 ml, heat to 80°, and add a solution of α-nitroso-β-naphthol, in 50 per cent acetic acid, until no further precipitation takes place. Cool, and make sure that no more precipitate is formed by adding a little more of the reagent. Filter after 2–3 hours into a Gooch crucible and wash with 12 per cent hydrochloric acid until all the nickel is removed. Finish washing with hot water. Dry, sprinkle a little pure oxalic acid upon the precipitate to prevent too sudden combustion during the heating, and heat very slowly to redness in an electric oven. Cool, place the crucible on a larger porcelain crucible with a perforated cover, and heat in a stream of hydrogen until the cobalt oxide is reduced to metal. Cool in hydrogen and weigh as Co. In another sample determine the nickel with dimethylglyoxime (p. 139).

See p. 146 for a procedure using α-nitro-β-naphthol in place of the nitroso compound.

Separation of Nickel from Zinc. Method of Tschugaeff-Brunck†

Treat the solution with ammonium chloride, and add enough ammonia to make slightly ammoniacal; no precipitate will be formed if

* *Ber.*, **18**, 699 (1885).

† *Z. angew. Chem.*, **1907**, 1849.

sufficient ammonium chloride has been added. Make slightly acid with hydrochloric acid, heat to boiling, and precipitate the nickel with an alcoholic 1 per cent dimethylglyoxime solution exactly as outlined on p. 139.

In the filtrate, it is best to precipitate the zinc as sulfide by acidifying with acetic acid and saturating the hot solution with hydrogen sulfide (cf. p. 150).

Remark. — When considerable zinc is present it is necessary to add more dimethylglyoxime to precipitate the nickel.

Separation of Nickel from Manganese. Method of Tschugaeff-Brunck*

Carry out the analysis exactly as described above with the only difference that the final precipitation should take place in an acetic acid solution. Neutralize the greater part of any mineral acid present with ammonia, treat the barely acid solution with 1 per cent dimethylglyoxime solution, and then, after the precipitate has formed, add sodium acetate and continue the analysis according to p. 139. If the alkali acetate is added before the dimethylglyoxime, a very voluminous precipitate is formed which, to be sure, can be filtered with suction, but even then the filtration is tedious. Thus, when possible, it is best to add the sodium acetate *after* the dimethylglyoxime. If, on the other hand, iron has been removed by a basic acetate separation and nickel and manganese are to be determined in the filtrate, the precipitation must take place in a solution already containing sodium acetate. In the filtrate from the nickel dimethylglyoxime precipitation, precipitate the manganese with ammonium sulfide and determine as described on p. 135.

Separation of Nickel from Iron

If the iron is present in the ferrous condition, oxidize it by boiling with nitric acid. Then dilute to 300 ml, add 1–3 g of tartaric acid, and make the solution ammoniacal to find out whether enough tartaric acid has been added (the solution must remain perfectly clear). Make slightly acid with hydrochloric acid, precipitate the nickel with dimethylglyoxime, carefully neutralize the acid with ammonia, and continue the analysis according to p. 140.

Determination of Nickel in Steel†

Procedure. — Dissolve 0.5 of steel in 20 ml of 6 N hydrochloric acid. To the resulting solution add 5 ml of concentrated nitric acid and boil

* *Z. angew. Chem.*, **1907**, 1849.

† O. Brunck, *Stahl und Eisen*, **28**, 331.

2 minutes to oxidize iron. Dilute to 100 ml and filter if there is any perceptible residue. Add 3 g of tartaric acid and make the solution ammoniacal and then barely acid with acetic acid. Dilute to 300 ml, heat nearly to boiling, and treat with 30 ml of a 1 per cent alcoholic solution of dimethylglyoxime.* Finally make slightly ammoniacal, adding enough ammonia to make the solution barely smell of this reagent. Allow the solution to stand in a warm place for 15 minutes and then cool for half an hour or longer. Finally filter the solution through a Gooch or Munroe crucible, wash thoroughly with hot water, dry at 105° for 90 minutes, and weigh as $Ni(C_4H_7N_2O_2)_2$. To the filtrate add 10 ml more of dimethylglyoxime reagent and make sure that the solution is barely alkaline. There should be no further precipitation.

By this method the nickel in a sample of steel can be determined within about 2 hours. The results are accurate, but lower than are sometimes obtained in practice when the cobalt is determined with the nickel. The precipitate is too voluminous to handle easily when the solution contains more than 0.1 g of nickel.

Removal of Ferric Chloride by Ether, Method of Rothe†

The fact that ferric chloride dissolved in hydrochloric acid, *d.* 1.1, is more soluble in ether than in this acid, is often taken advantage of in the determination of metals such as nickel, manganese, cobalt, copper, aluminum, titanium, vanadium, and chromium in samples of steel. It has also been used for the determination of sulfur in steel after oxidation to sulfuric acid, which does not dissolve in the ether. The underlying principle is the same as that governing the distribution of iodine between water and carbon disulfide (see Vol. I). An example will be given of such a process in the following method for determining manganese in steel. Beryllium chloride as well as molybdic acid follow the ferric chloride and dissolve in the ether.

Determination of Manganese in Iron and Steel

Requirements. — 1. Hydrochloric acid, *d.* 1.10.

2. Ether-hydrochloric acid. To concentrated hydrochloric acid, *d.* 1.19, add ether in small portions until, after shaking, a layer of ether is on top of the acid. One volume of concentrated acid dissolves about 1.5 volumes of ether.

* The volume of the alcoholic solution should in no case be more than half that of the nickel solution, as the precipitate is slightly soluble in alcohol. About 0.4 g of the glyoxime should be used for each 0.1 g of nickel. A deep red color in the solution shows that ferrous iron is present.

† *Z. anal. Chem.*, **1901**, 809.

3. Dilute ether-hydrochloric acid. To approximately $6N$ hydrochloric acid, *d.* 1.10, add ether in the same way. One volume of the acid dissolves about 0.5 volume of ether.

4. A shaking funnel similar to that shown in Fig. 40. The analysis can be made with two ordinary separatory funnels, but this funnel recommended by Rothe is well adapted to this work.

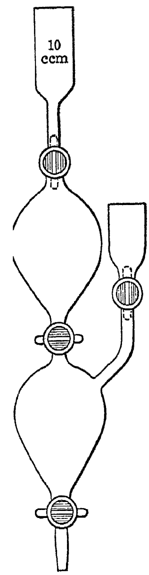

FIG. 40.

Procedure. — If the iron or steel contains less than 1 per cent manganese, take 10 g of sample for analysis, otherwise a correspondingly smaller quantity. Dissolve the sample in a 500-ml beaker with $7.5N$ nitric acid, using 15 ml of the acid for each gram of metal. As soon as the violent reaction is over, heat over a wire gauze until all the iron has gone into solution and no more brown fumes are evolved. Evaporate the solution to dryness and gently bake the residue. Take up in 50 ml of $6N$ hydrochloric acid, heating until all the ferric oxide and basic salt has dissolved. Then dilute to 150 ml and filter off the silica.

Evaporate the filtrate nearly to dryness; a thick sirupy liquid should remain but there should be no deposition of crystals. Pour this solution into the upper bulb of the funnel shown in Fig. 40, and rinse out the dish with hydrochloric acid, *d.* 1.10, until no yellow coloration is produced on pouring the acid into the dish. Ten or fifteen milliliters of the acid, added in 3-ml portions, should accomplish this rinsing of the dish. Shake the solution to mix it well, and cool under the water faucet. Then, for each gram of metal taken, add 6 ml of the concentrated acid that has been saturated with ether. Mix, cool again, and nearly fill the upper bulb with pure ether. Close the stopcock and shake well, cooling from time to time under running water. Fasten the shaking funnel to a ring stand in a vertical position and allow the liquid in the bulb to separate into two layers. The upper, ether layer will contain the greater part of the iron, and the lower acid will contain all the manganese.

Transfer the lower layer to the lower bulb of the shaking funnel without letting any of the upper layer flow into the boring of the stopcock that separates the two bulbs. After a few minutes a little acid will separate out below the ether. Allow this also to run into the lower bulb. To rinse the boring add 3 ml of the dilute ether-hydrochloric acid mixture and again drain off the lower layer of liquid into the bottom bulb. Now add 10 ml of the dilute ether-acid mixture to the upper bulb and nearly fill the lower bulb with ether. Shake well. Then draw

off the lower layer of the liquid in the lower bulb into a porcelain dish, drain off the lower layer of the upper bulb into the lower bulb, and rinse the upper bulb with a little of the dilute ether-acid mixture. Withdraw the lower layer of the upper bulb into the lower bulb and the lower layer of the bottom bulb into the dish. Repeat this washing of the apparatus 3 or 4 times and then it can be assumed that all the manganese, together with the nickel, cobalt, aluminum, chromium, sulfuric acid, and phosphoric acid is in the dish.

From this solution, evaporate off the ether on a warm water-bath, taking care not to boil the solution or to have a lighted flame very near. Finally evaporate to dryness and take up in 5 ml 6 N hydrochloric acid. Dilute to 100 ml and precipitate the copper with hydrogen sulfide. Filter and wash as described under Copper.

Bauer and Deiss recommend the following treatment to separate the manganese from the remaining elements: Add a little sulfuric acid to the filtrate from the copper precipitate and evaporate to dryness, finally heating until the excess acid is all expelled. Cover the sulfates in a platinum dish with a solution of 2–5 g of pure sodium hydroxide dissolved in a little water. Evaporate to dryness and carefully heat over a free flame until the sodium salt fuses, keeping the dish in motion. Cool, sprinkle a little sodium peroxide over the mass, and again carefully heat until the mass fuses. Avoid injuring the dish by not overheating any part of it. Cool, cover the dish with a watch glass, and digest the fused mass with 60 ml of hot water. After again cooling, add a little more sodium peroxide to make sure that all the green sodium manganate is decomposed and hydrated manganese dioxide precipitated. Heat to decompose the excess of sodium peroxide for about an hour on the water-bath. Rinse the contents of the dish into a beaker. Dilute to 200 ml and allow the precipitate to settle; it contains all the manganese, nickel, and cobalt and some iron that was not removed by the ether. If a stain remains on the sides of the platinum dish, dissolve it with a few drops of hydrochloric acid, dilute, add sodium peroxide, heat to decompose the excess, and rinse into the beaker.

Filter and wash the precipitate with water containing 2 per cent of dissolved ammonium sulfate. The filtrate will contain all the chromium as chromate and the aluminum as aluminate besides alkali phosphate and other alkali salts.

Dissolve the moist precipitate in hot 3 N hydrochloric acid and precipitate the iron by the basic acetate procedure (p. 159). If a large precipitate is obtained, dissolve it in hydrochloric acid and repeat the basic acetate precipitation.

To remove the nickel and cobalt from the filtrate, add a drop of 6 *N* acetic acid and saturate the solution with hydrogen sulfide. Heat to boiling, and after the precipitate has settled, filter off the nickel and cobalt sulfides. Evaporate the filtrate to a small volume and precipitate the manganese by bromine, as described on p. 136, and determine as Mn_3O_4 or as $MnSO_4$.

This method is described in detail because it is capable of giving excellent results. It is well to have accurate gravimetric methods for the determination of constituents which are usually determined by the more rapid and far simpler volumetric methods. In this way a check is obtained upon the accuracy of the volumetric methods.

The Use of Tannin in Quantitative Analysis

General Principles. — The name *tannin* has been given to a widely disseminated group of organic substances that are capable of converting raw animal hides into leather. Common tannin, or gallotannic acid, $C_{14}H_{10}O_9 \cdot 2H_2O$, is obtained from gall nuts. It has an astringent taste and the character of a weak acid. Its aqueous solution is really a colloidal suspension of negatively charged particles and will form precipitates, or gels, with positively charged suspensions of certain inorganic compounds by reciprocal flocculation (see Vol. I). The resulting adsorption complexes are voluminous and characteristic precipitates which filter well; upon ignition they yield oxide of a metal in a weighable form.

Tannin as a reagent in quantitative analysis was recommended by Powell and Schoeller for separating tantalum from columbium,* and the use of this reagent was extended by them and their collaborators to the determination of other elements (Ti, Zr, Th, Al, U, and W).† Subsequently Moser and his students studied the use of tannin in the analytical chemistry of beryllium and of gallium.‡

The importance of tannin as a precipitant for aluminum, zirconium, hafnium, thorium, uranium, titanium, columbium, and tantalum is due to the following facts. (1) Under proper conditions the precipitates can be formed from tartrate solutions, which is not the case with respect to the precipitation of the hydroxides by ammonia (cf. p. 114). Tannin is a general precipitant for the above elements (formerly called *earths*) just as hydrogen sulfide is for the heavy metals. (2) In an oxalate solution, a separation into two classes can be made just as with ammonium polysulfide in the analysis of sulfides. Here also one of the groups represents oxides which are acid in nature (Ta_2O_5, Cb_2O_5, TiO_2), and the other group oxides which are more basic (ZrO_2, HfO_2, ThO_2, Al_2O_3, BeO, UO_3, Cr_2O_3, etc.). (3) The colored tannin precipitates are characteristic just as are the colored sulfides. (4) With the aid of tannin, excellent separations can be made of (*a*) tantalum from columbium in all proportions and (*b*) small quantities of tantalum and columbium from larger quantities of titanium.

Reagent. — Use a freshly prepared 2 to 5 per cent solution of high-grade, com-

* *Analyst*, **50**, 485 (1925).

† *Ibid.*, **52**, 504 (1927); **54**, 709 (1929); **57**, 550 (1932); **58**, 143 (1933).

‡ *Monatsh.*, **48**, 113, 673 (1927); **50**, 181 (1928); **51**, 181, 325 (1929).

mercial gallotannic acid (tannin) in boiling-hot distilled water. The tannin should be practically ash-free.

The following eight procedures illustrate the use of tannin in quantitative analysis.

1. Precipitation of Aluminum, Zirconium, Thorium, Uranium, Titanium, Columbium, and Tantalum from Tartrate Solution*

Fuse 0.25 g or less of the oxides in a silica crucible with 3 to 4 g of potassium bisulfate (cf. p. 120). Dissolve the cold, fused mass in a strong solution containing 3 g of tartaric acid. Repeat the fusion if necessary. Into 200 ml of the acid tartrate solution thus obtained, introduce hydrogen sulfide and add 10 g of NH_4Cl and 10 g of ammonium acetate. Allow the solution to stand for some time in a warm place after saturating with hydrogen sulfide, to allow Fe_2S_3 to flocculate. Filter, wash the precipitate with water containing a little ammonium sulfide and chloride. Boil the filtrate to decompose the ammonium sulfide present and add acetic acid dropwise until the 300 to 500 ml of solution is faintly acid. Heat to boiling, and while boiling introduce tannin solution (1 to 3 g of tannin). Keep the solution on a covered water-bath for an hour and filter, with the aid of gentle suction, through an 11-cm washed filter supported on a filtering cone. Before the precipitate becomes compressed and furrowed by suction, rinse it back to the original beaker with a liberal stream of wash liquor (2 per cent NH_4Cl solution containing a little tannin). Churn up the precipitate with some ashless filter pulp (p. 98), return to the filter, wash thoroughly with the wash liquor, and use a rubber policeman and a little paper pulp to remove the last traces of precipitate from the walls of the beaker.

If the precipitate is not very bulky, the use of suction is unnecessary.

Dry the washed precipitate in a crucible placed on an asbestos mat until the paper is well charred (cf. p. 39), and then ignite with the crucible on a triangle. Cool the crucible, cover with a watch glass, and half fill it with 0.5 N HCl. Heat half an hour on the steam-bath, make the resulting solution alkaline to methyl red by adding ammonia, filter, wash with 2 per cent ammonium nitrate solution, and ignite to constant weight of oxides.

The leaching of the precipitate after the first ignition ensures the complete removal of alkali salts and of sulfate; this is difficult to effect with bulky precipitates.

The filtrate from the tannin precipitate should be tested for complete precipitation as follows: Heat to boiling, treat with 0.5 g of tannin, and make feebly ammoniacal. This causes the formation of a discolored precipitate, which should be soluble on slight re-acidification, leaving only small dark flocks of organic matter. If not,

* Schoeller and Webb, *Analyst*, **54**, 709 (1929).

the additional precipitate must be collected, washed, and added to the main precipitate.

The tannin complexes of Al, Zr, and Th are colorless; those of Ti and Cb, red; those of W and U, brown; and the Ta precipitate, yellow. Ferric salts give a precipitate of an intense purplish black color. The above procedure provides for the removal of iron as sulfide. Tungsten interferes because, although it is not precipitated alone by tannin from tartrate or oxalate solutions, it is adsorbed to a considerable extent by the other precipitates.

2. Separation of Iron from Aluminum*

The above method is a reliable and convenient means for separating iron from less than 0.05 g of alumina. The alumina-tannin complex is too bulky to handle when larger quantities of alumina are present, and in such cases an aliquot part of the solution should be taken. The weight of tannin used should be at least 20 times that of the Al_2O_3 obtained by igniting the tannin precipitate; at least 0.5 g of tannin should always be used.

3. Separation of the Acid Tannin Group (TiO_2, Ta_2O_5, Cb_2O_5) from the Basic Tannin Group (Al_2O_3, ZrO_2, ThO_2, UO_3, BeO)†

Principle. — The members of the "acid tannin group" are precipitated as tannin complexes in a feebly acid oxalate solution which is half-saturated with ammonium chloride; the members of the basic tannin group are not precipitated unless ammonia is added. The process gives a clean-cut separation of any one or all of the members of one group from one or more members of the other.

Procedure. — Fuse the mixed oxides (up to 0.25 g) with potassium acid sulfate as in the first procedure. Dissolve the cold, fused mass in 75 to 100 ml of saturated ammonium oxalate solution. To the boiling solution add N NH_4OH until a faint cloudiness forms, and at once dissolve this in as little HCl as possible; the solution should now be acid to litmus. Add an equal volume of saturated NH_4Cl solution and continue boiling while introducing dropwise a fresh 4 per cent solution of tannin. The quantity of tannin used should be 10 to 12 times the weight of "acid oxides" present.

Allow the tannin precipitate to stand on a hot plate for an hour before filtering. Filter the precipitate as directed on p. 176 in Method 1, but this time use as wash liquor a solution containing 5 per cent NH_4Cl and 1 per cent $(NH_4)_2C_2O_4$. Ignite the washed precipitate in a tared porcelain crucible.

Always test the filtrate for complete precipitation as follows: Heat to boiling, neutralize with N NH_4OH, and treat with tannin dropwise until a slight precipitate is formed. If this is grayish or brownish gray, and soluble on slight acidification, the precipitation of the "acid group" is complete; if yellow or pale orange in color, some of the "acid group" remains. In this case, add tannin under the conditions given above and add the new precipitate to that previously obtained.

To test the weighed precipitate of "acid oxides" for members of the "basic"

* Schoeller and Webb, *loc. cit.*

† Schoeller and Powell, *Analyst*, **57**, 550 (1932).

group, repeat the entire procedure using the same quantity of tannin as in the first case. The weight of the new precipitate should be substantially the same as that obtained in the first place. Leach these oxides with 0.5 N HCl and continue as in Method 1 and finally obtain a weight of purified oxides.

Then, to determine oxides of the "basic" group, take the combined filtrates from the tannin precipitations, add more tannin to the boiling solution and a moderate excess of ammonia. Filter off the tannin precipitate, wash it with 2 per cent NH_4Cl solution, and ignite to constant weight of oxides. This weight is usually somewhat high owing to a little SiO_2 from the vessels used in the analysis or from the reagents. To correct for this, fuse with $KHSO_4$, dissolve the melt in 0.5 N H_2SO_4, filter off the insoluble residue, ignite, and call it SiO_2. Make a corresponding reduction from the weight of the "basic" oxides.

4. Separation of Tantalum from Columbium*

Principle. — Tantalum and columbium are precipitated completely from an oxalate solution on adding an excess of tannin solution and neutralizing with ammonia (see **3**); by properly regulating the quantities of reagents, it is possible to accomplish a quantitative separation of these two elements. Tantalum requires less tannin than columbium does and the precipitate forms in a more acid solution. The tantalum complex is yellow and the columbium complex is red; co-precipitation of the columbium with tantalum is indicated by the orange-yellow to orange-red color of the tannin precipitate. The progress of the precipitation, therefore, can be controlled by watching the color of the precipitate. It is impossible, however, to effect a quantitative separation by means of a single precipitation if less tantalum than columbium is present.

Schoeller has devised a scheme of analysis which furnishes (1) a yellow tannin precipitate containing tantalum and no columbium (2) an orange to red precipitate containing both tantalum and columbium, and (3) a filtrate containing columbium and no tantalum. A complete separation is accomplished by systematic retreatment of the orange to red precipitate whereby three fractions are obtained again, the middle fraction is fractionated, and the process repeated until finally all the tantalum is obtained in the form of a yellow tannin precipitate. The actual working out of the method involves directions which are too lengthy to be given here; the original paper should be consulted for details.

5. Separation of Small Quantities of Tantalum and Columbium from Titanium†

Principle. — Titanium oxide is amphoteric and forms a sulfate, whereas the earth acids, Ta_2O_5 and Cb_2O_5, do not. A solution of tannin in dilute sulfuric acid, placed in contact with the product formed by fusing TiO_2, Ta_2O_5, and Cb_2O_5 with $KHSO_4$, dissolves $Ti(SO_4)_2$, leaving behind the Ta_2O_5 and Cb_2O_5. If tannin is not present, all three oxides dissolve in the sulfuric acid.

Procedure. — Fuse 0.1 to 0.25 g of the mixed oxides with 2 to 3 g of $KHSO_4$ in a silica crucible and make the melt solidify around the sides

* Schoeller, *Analyst*, **57**, 750 (1932).
† Schoeller, *ibid.*, **54**, 453 (1934).

of the crucible. Pour some of the hot reagent (1 per cent tannin in 1.8 N H_2SO_4) into the crucible and heat gently until the melt becomes detached. Transfer the contents of the crucible to a small beaker, rinse out the crucible with more of the hot reagent, heat the liquid just to boiling, and then, without further heating, allow the mixture to stand for some hours or over night. Filter, wash the residue with 0.5 N H_2SO_4 containing a little tannin, ignite, and weigh the residual Ta_2O_5 and Cb_2O_5.*

If the weighed oxides are again fused with a small amount of $KHSO_4$ and the melt dissolved in a little tartaric acid solution, then on boiling with one-quarter the liquid's volume of concentrated sulfuric acid, a characteristic, white precipitate of earth acids will be obtained (cf. Vol. I).

The above process is very simple and rapid but not suitable for the separation of large quantities of earth acids from titania. In such cases recourse must be had to the oxalate-salicylate method.† In principle, this method consists in dissolving the bisulfate melt of the mixed oxides in ammonium oxalate solution and adding an excess of sodium salicylate, whereby the titanium is converted into soluble, orange-colored sodium titanylsalicylate. The solution is then precipitated with excess of calcium chloride, the precipitated calcium oxalate carrying down the insoluble salicylic complexes of the earth acids.

6. Determination of Small Quantities of Tungstic Acid‡

Principle. — When a dilute solution of sodium tungstate containing sodium or ammonium chloride is treated with tannin, and acidified, the tungstic acid is precipitated as the brown tannin complex. A small part of the tungsten complex remains in colloidal suspension. Addition of the salt of an alkaloid such as cinchonine produces a flocculent cinchonine tannin complex which acts as a collector of the colloidal tungsten precipitate.

This method replaces the mercurous nitrate precipitation process; it solves the problem of the recovery of small quantities of tungstic acid from solution. It is also to be preferred to the cinchonine precipitation method, which gives low results in the presence of much alkali salt.

Procedure. — To 100–150 ml of slightly alkaline solution, such as is obtained after fusing with Na_2CO_3 and extracting with water, add dilute HCl until neutral to phenolphthalein and a fresh solution of 0.5 g tannin in a little water. Part of the tannin will form a white turbidity if much chloride is present. Now make acid to litmus paper, which will cause the brown WO_3 and tannin complex to appear. After a few minutes, heat to gentle boiling and add 10 ml of 2.5 per cent cinchonine solution. Boil 5 minutes longer, and let stand 6 hours or over night.

* If the proportion of titania in the mixed oxides is very high, the pentoxides should be retreated.

† Schoeller and Jahn, *Analyst*, **57**, 72 (1932).

‡ Schoeller and Jahn, *ibid.*, **52**, 504 (1927).

Filter with the aid of filter-paper pulp and wash with a cold 5 per cent NH_4Cl solution containing a little tannin. Pay no attention to a white turbidity that may form in the filtrate. Ignite in a tared porcelain crucible, and weigh the residual WO_3.

7. Beryllium

Beryllium belongs to a third tannin group, the members of which (Be, Mn, Ce, and Y furnish tannin complexes precipitated in the presence of an excess of ammonia, and soluble in dilute acetic acid).*

Moser and List† base a separation of beryllium from a number of metals of Group III upon the solubility of its tannin complex in acetic acid. The solution is treated with hydrogen sulfide for the removal of heavy metals, and the filtrate is boiled with addition of bromine for the oxidation of ferrous iron. After neutralization with sodium carbonate, the solution is hydrolyzed in the presence of ammonium nitrite and methyl alcohol (p. 97). The precipitate, which contains beryllia and sesquioxides and dioxides of Group III, is dissolved in nitric acid. The solution is neutralized with ammonia, treated with ammonium acetate and nitrate, and acidified with acetic acid. Addition of tannin to the boiling solution precipitates Al, Cr, Fe, Ga, Ti, Zr, and V. Beryllium passes into the filtrate, from which it is recovered by tannin and an excess of ammonia.

8. Gallium

Moser and Brukl‡ found tannin to be the best and most sensitive precipitant for gallium. The boiling, weakly acid acetate solution containing 2 per cent of ammonium nitrate is treated drop by drop with 10 per cent tannin solution while stirring. At least 0.5 g of tannin should be added. The bulky precipitate is washed with hot water containing a little ammonium nitrate and acetic acid, and ignited to Ga_2O_3. The procedure separates gallium from zinc, which is of practical importance because gallium occurs in zinc ores. The separation of gallium from aluminum is effected with cupferron.§

* Schoeller and Webb, *Analyst*, **59**, 669 (1934).

† *Monatsh.*, **51**, 181 (1929).

‡ *Ibid.*, **50**, 181 (1928).

§ *Ibid.*, **51**, 325 (1929).

METALS OF GROUP II

MERCURY, LEAD, BISMUTH, COPPER, CADMIUM, ARSENIC, ANTIMONY, TIN (PLATINUM, GOLD, SELENIUM, TELLURIUM, MOLYBDENUM, GERMANIUM, TUNGSTEN, AND VANADIUM)

A. SULFO-BASES

MERCURY, LEAD, BISMUTH, COPPER, CADMIUM

MERCURY, Hg. At. Wt. 200.6

Forms: HgS, Hg_2Cl_2, and Hg

Determination as Sulfide

(*a*) *Precipitation with Hydrogen Sulfide*

The solution should contain not over 0.1 g of mercury as *mercuric* salt in a volume of 100 ml and should contain no oxidizing substances ($FeCl_3$, Cl, much HNO_3, etc.). Saturate with hydrogen sulfide in the cold, allow the precipitate to settle, filter through a Gooch crucible, wash with cold water, dry at 105°–110° C, and weigh as HgS.

Remark. — This method affords excellent results and should be used whenever possible. Unfortunately, however, it is not always applicable, for most solutions to be analyzed contain strong nitric acid (obtained by the solution of impure mercuric sulfide in aqua regia, by the decomposition of organic mercury compounds by the method of Carius, or by the oxidation of mercurous salts). It is not possible to expel the excess of nitric acid by evaporating the solution with hydrochloric acid, because considerable amounts of mercuric chloride are volatilized with the escaping steam. In such a case the following procedure suggested by Volhard should be used:

(*b*) *Precipitation with Ammonium Sulfide*

Nearly neutralize the acid solution of the mercuric salt with pure sodium carbonate and treat with a slight excess of freshly prepared ammonium sulfide. Add pure sodium hydroxide solution (free from Ag, Al_2O_3, and SiO_2) while rotating the solution, until the dark liquid begins to lighten; then heat to boiling and add more sodium hydroxide until the liquid is perfectly clear. The solution now contains the mercury as sulfo-salt, $Hg\langle{}^{SNa}_{SNa}$. Add ammonium nitrate (5 g for each 100 ml), boil the solution until the ammonia is almost entirely expelled, and allow the precipitate to settle. By means of the boiling with ammonium nitrate, the sulfo-salt is decomposed according to the equation:

$$Hg(SNa)_2 + 2\,NH_4NO_3 = 2\,NaNO_3 + (NH_4)_2S + HgS$$

Decant the clear
precipitate by deca
longer reacts with

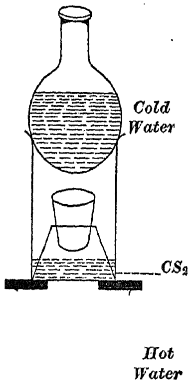

FIG. 41.

the precipitate contains free sulfur, boil it with a little sodium sulfite before filtering.*

A still better way of removing free sulfur from the precipitate consists of extracting with carbon bisulfide. In this case filter off the mercuric sulfide, together with the sulfur, through a Gooch crucible, wash thoroughly with water and then three times with alcohol. Now place the crucible upon a glass tripod in a beaker containing some carbon bisulfide (Fig. 41).† Support the beaker over a vessel filled with hot water and cover it with a round-bottomed flask containing cold water to serve as a condenser. After about an hour the sulfur will be completely extracted. Remove the carbon bisulfide from the precipitate by washing once with alcohol and once with ether. Drive off the ether by gently warming, dry the precipitate at 110° C, and weigh as HgS.

Determination of Mercury in Non-Electrolytes

If it is desired to determine mercury in an organic non-electrolyte, decompose the compound by the method of Carius (see Elementary Analysis) by heating in a closed tube with concentrated nitric acid, and precipitate the mercury as sulfide by the method of Volhard; or to the acid solution add pure sodium hydroxide solution to alkaline reaction and then enough pure potassium cyanide to dissolve the mercuric oxide. Now saturate the solution with hydrogen sulfide, add ammonium acetate, boil the solution until the ammonia is almost entirely expelled, allow the precipitate to settle, filter, and wash first with hot water, then with hot dilute hydrochloric acid, and finally with water. After drying at 110° C, weigh the precipitate of mercuric sulfide.

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* By boiling with sodium sulfite, the sulfur is changed to sodium thiosulfate, $Na_2SO_3 + S = Na_2S_2O_3$.

† G. Vortmann, *Uebungsbeispiele aus der quantitativen chemischen Analyse*, p. 28, Vienna, 1899.

Determination as Mercurous Chloride

For the analysis of a solution containing a *mercurous* salt, treat the solution, at a volume of 100 ml for each 0.1 g of mercury, with a slight excess of sodium chloride solution. After standing 12 hours filter through a Gooch crucible, dry at 105° C, and weigh as Hg_2Cl_2. If the solution contains a mercuric salt, first reduce it by the method of H. Rose, using phosphorous acid in the presence of hydrochloric acid as follows:

To the solution of *mercuric* salt (which almost always contains nitric acid) add some hydrochloric acid, enough water to make the volume at least 100 ml for each 0.1 g of mercury, and an excess of phosphorous acid. After standing for 12 hours filter off the precipitate through a Gooch crucible, dry at 105°, and weigh.

Remark. — The results obtained by this method are always about 0.4 per cent too low, but in spite of this fact the method is to be recommended.

The phosphorous acid necessary for this method can be obtained by the oxidation of phosphorus in moist air or by the decomposition of phosphorus trichloride with water, evaporating the solution to remove the hydrochloric acid and dissolving the residue in water.

Determination as Metal

Nearly all mercury compounds except the iodide are decomposed quantitatively by heating with lime:

$$2\,HgX + 2\,CaO = 2\,CaX + 2\,Hg + O_2$$

To carry out this determination,* take a glass tube 50 cm long and 1.5 cm wide, open at both ends, and near one end place an asbestos plug, follow this with an 8-cm layer of pure lime, then an intimate mixture of a weighed amount of substance with lime, and finally a layer of lime 30 cm long. At the other end of the tube insert another asbestos plug. After the tube has been filled, draw out the tube at the end nearest this second asbestos plug until it is only 4 cm wide. Connect this end of the tube by means of rubber tubing with the empty, narrower arm of a very small Péligot tube. Loosely fill the other and wider end of the Péligot tube with pure gold-leaf. Place the glass tube in a combustion-furnace and pass illuminating-gas (carbon dioxide is less suited) through it for half an hour. Then heat the tube, at first where the 30-cm layer of lime is, then light the other burners one after another until finally the entire contents of the tube are subjected to gentle ignition. During the whole of the operation pass illuminating-gas through the apparatus at the rate of about three bubbles a second. The greater part of the mercury collects in the lower empty end of the

* First proposed by Erdmann and Marchand, *J. prakt. Chem.*, **31**, 385.

Péligot tube, and the mercury vapors, that are carried further, amalgamate with the gold. A small amount of the mercury condenses in the drawn-out tube. After cooling the apparatus (in a current of illuminating-gas) cut off the narrow part of the tube both sides of the condensed mercury and weigh. Then heat gently, while passing air through the tube to volatilize the mercury and again weigh. The difference in weight gives the amount of mercury condensed in the combustion tube. The Péligot tube is usually moist; pass dry air through it for some time, and finally weigh it. The gain in weight represents the weight of mercury that amalgamated with the gold.

Although it is easy to obtain good results by this method, it is slower than the sulfide method and is no more accurate.

If it is desired to determine the amount of mercury vapor present in a given space, it is only necessary to aspirate the gas through a calcium-chloride tube filled with gold-leaf. The gain in weight of the latter shows the amount of mercury present in the gas.

Electrolytic Determination of Mercury*

Mercury can be determined satisfactorily by the electrolysis of acid, neutral, or alkaline solutions. The metal is deposited in the form of little drops, which, when the quantity is small, adhere to the electrode, or, when larger amounts are present, the mercury may collect at the bottom of the platinum dish used as cathode.

The electrolysis takes place to advantage in solutions slightly acid with nitric acid.

Procedure. — To 150 ml of the neutral or slightly acid solution of the mercurous or mercuric salt in a beaker, add 2 or 3 ml of concentrated nitric acid, and electrolyze with a platinum gauze electrode at room temperature with a current of 0.05–0.10 ampere. The voltage should be between 3.5 and 5 volts. If the electrolysis is started at night, it will be finished next morning, provided the amount of mercury does not exceed 1 g. By using a current of 0.6–1 ampere the electrolysis is finished at the end of 2 or 3 hours. At the end of the electrolysis, wash the metal with water without interrupting the current, then with alcohol,† and dry by touching it with filter paper. Finally keep it in a desiccator‡ over fused potassium hydroxide and a small dish of mercury

* Luckow, *Z. anal. Chem.*, **19**, 15 (1880); Smith and Knerr, *Am. Chem. J.*, **8**, 206; F. W. Clarke, *Ber.*, **11**, 1409 (1878); Rüdorff, *Z. angew. Chem.*, **1894**, 388; Classen and Ludwig, *Ber.*, **19**, 324 (1886); G. Vortmann, *Ber.*, **24**, 2750 (1891).

† It is usually stated that alcohol is not to be used, but with gauze electrodes it does no harm.

‡ Private communication from A. Miolati, cf. Borelli, *Revisto tecnica*, V, Part 7 (1905). Even at 20° the tension of mercury vapor is considerable. It amounts to 0.00133 mm.

for several hours. In this way correct results are obtained. Drying at 100° and then over sulfuric acid in a desiccator gives rise to low results because the acid absorbs considerable mercury vapor.

During the electrolysis of mercuric chloride* the solution often becomes turbid in consequence of the formation of insoluble mercurous chloride; this does no harm, however, as the metal is subsequently deposited on the cathode.

Mercury can also be electrolyzed from a solution in potassium cyanide in the presence of some caustic alkali, and similarly from a solution formed by dissolving mercuric sulfide in 50–60 ml of concentrated sodium sulfide solution.

The great advantage of the electrolytic determination of mercury lies in the fact that good deposits are obtained irrespective of the nature of the acid radical, or element, which is combined with mercury.

LEAD, Pb. At. Wt. 207.2

Forms: PbO, $PbSO_4$, PbO_2, and in rare cases $PbCl_2$†

1. Determination as Lead Oxide, PbO

If the lead is present as carbonate, nitrate, or peroxide, it is only necessary to ignite a weighed portion in a porcelain crucible over a small flame and weigh the residue. The treatment of the nitrate requires care, because on rapid ignition the mass decrepitates.

2. Determination as Lead Sulfate, $PbSO_4$

If the lead is present in solution in the form of its chloride or nitrate, add an excess of dilute sulfuric acid‡ and evaporate the mixture on the water-bath as far as possible, then over a free flame until dense white fumes of sulfuric acid are evolved. Cool, dilute with 15 volumes of water, stir, allow to stand some hours, and filter through a Gooch cru-

* In the electrolysis of the chloride, it is better to use a platinum dish with dull, unpolished inner surface (Classen) because then any mercurous chloride will certainly be reduced to metal, which is not always the case with gauze electrodes. When a dish is used as cathode, wash the electrode with water, without breaking the current, by pouring water into it from a wash-bottle while the solution is being siphoned off. As soon as the ammeter (or voltmeter used as an ammeter) reaches the zero-mark, the washing is finished. Turn off the current, pour off the solution carefully, dry the electrode as above and weigh.

† See Analysis of Vanadinite.

‡ The solution at the time of filtering should contain about 5 per cent of free sulfuric acid.

cible. Wash at first with 8 per cent sulfuric acid (by weight), then with alcohol, and dry at 100°. Place the Gooch crucible in a larger porcelain crucible, provided with an asbestos ring, and ignite over the full flame of a Teclu or Tirrell burner.

If it is desired to use an ordinary filter, finally wash the precipitate with alcohol until the wash liquid no longer gives the sulfuric acid reaction, dry, transfer as much of it as possible to a piece of glazed paper, and cover it with a watch glass. Ignite the paper together with some precipitate in a tared porcelain crucible. The hot carbon will reduce some of the $PbSO_4$ to Pb. Moisten with nitric acid and a drop of H_2SO_4, and heat carefully until all excess acid is evolved. Then add the bulk of the precipitate and heat again.

If the lead is originally present as acetate, treat the solution with an excess of dilute sulfuric acid and twice its volume of alcohol, filter after standing some hours, and treat the precipitate of lead sulfate exactly as described above.

To determine the lead present in organic compounds, place the substance in a large porcelain crucible, treat with an excess of concentrated sulfuric acid, and very cautiously heat in the covered crucible over a free flame until the sulfuric acid is completely expelled. Then gently ignite the crucible; if the residue is white, it is ready to be weighed. Otherwise add more sulfuric acid and repeat the process until finally a white residue is obtained.

If the organic lead compound is soluble in water, it is preferable first to precipitate the lead by means of hydrogen sulfide and then transform the precipitate into sulfate. For this purpose, place as much as possible of the washed and dried lead sulfide precipitate upon a watch glass, heat the filter and remainder of the precipitate in a large porcelain crucible, which is supported in an inclined position. Heat carefully over a small flame until the filter paper is completely consumed. Add the main part of the precipitate to the crucible, cover with a watch glass, and treat with concentrated nitric acid at the temperature of the water-bath. When the main reaction is over, repeat the treatment with strong nitric acid until the contents of the crucible are pure white in color. Then remove the watch glass, add 5 or 10 drops of dilute sulfuric acid, and evaporate the liquid as far as possible on the water-bath. Remove the excess of sulfuric acid by heating on the air-bath (cf. Fig. 14, p. 37), and weigh the lead sulfate. Should the precipitate be dark colored after the ignition, moisten it with concentrated sulfuric acid and again expel the excess of acid.

If the lead is present in an organic compound which is not capable of dissociation, the compound should be decomposed in a closed tube with strong nitric acid according to the method of Carius (see Determination of Chlorine), finally washing out the contents of the tube, adding sulfuric acid, and treating the precipitate as above described.

Separation of Lead Sulfate from Barium Sulfate and Silicic Acid

In the analysis of sulfide ores containing lead, it is customary to dissolve the finely powdered ore in nitric acid, or aqua regia, and to remove the volatile acids by evaporation with sulfuric acid, eventually heating over the free flame until fumes of sulfuric acid come off thickly. The sulfuric acid should be diluted with an equal volume of water before adding it to the original solution; usually 10 ml of the diluted acid is sufficient. After the evaporation, allow the moist residue to cool,

add 100 ml of water, and filter off the precipitate, washing it with 5 per cent sulfuric acid. The precipitate contains all the lead as sulfate but often contains silica and barium sulfate (also strontium sulfate and sometimes calcium sulfate). If only a little impurity is present, treat the precipitate with hot ammonium acetate solution (made by neutralizing $6\,N$ acetic acid with $6\,N$ ammonia, and leaving the mixture barely ammoniacal). When the precipitate is large in amount it is best to wash it into a beaker or flask and heat it with about 20 ml of $2\,N$ ammonium acetate solution (or enough to dissolve all the lead sulfate), then filter through the original filter, and wash with hot ammonium acetate solution and finally with hot water until the filtrate gives no blackening with ammonium sulfide. Small precipitates of lead sulfate can be dissolved on the filter. The silica and barium sulfate will remain undissolved, but calcium sulfate will follow the lead sulfate.

To obtain lead from the acetate solution, precipitate it as sulfide by hydrogen sulfide, and transform, after drying, into sulfate as described on p. 186. Or add 10 ml of $18\,N$ sulfuric acid to 100 ml of the ammonium acetate solution, remove the acetic acid by evaporation, allow the residue to cool, dilute with water to 100 ml, and filter the lead sulfate into a Gooch crucible. Wash the precipitate with cold 5 per cent sulfuric acid, heat in an air-bath, and weigh.

If the amount of ammonium acetate solution used is not too large, the lead may be precipitated by adding enough sulfuric acid to the acetate solution to make the solution contain from 5 to 10 per cent sulfuric acid by weight. Sometimes the precipitate is not pure lead sulfate, in which case it should be redissolved in ammonium acetate and the precipitation as sulfate repeated.

With lead ores containing more substantial amounts of alkaline-earth sulfates, evaporation of the nitric solution of the ore with sulfuric acid gives a residue of sulfates containing a variable amount of lead in the form of a mixed precipitate $(Ba, Pb)SO_4$, insoluble in ammonium acetate. Such ores should be decomposed with hydrochloric and a little nitric acid, the liquid evaporated to dryness, the residue digested with 20 ml of strong hydrochloric acid, and the acid diluted to 200 ml with hot water. Then, after filtering and thoroughly washing with hot water to dissolve all the lead chloride, the silica and barium sulfate will remain insoluble. Treat the filtrate with hydrogen sulfide to precipitate PbS, and after extraction of antimony sulfide, etc., if present, with sodium sulfide, dissolve in HNO_3 and convert into sulfate as described in the preceding paragraph.

3. Electrolytic Determination of Lead as Peroxide (PbO_2)

Lead can be deposited as metal upon the cathode by the electrolysis of solutions containing the complex oxalate, the acetate, the hydroxide dissolved in caustic alkali or the phosphate dissolved either in caustic alkali or in phosphoric acid, *d.* 1.7. The deposit is easily oxidized, and there is always danger of some lead peroxide being formed on the anode. No method for the electrolytic determination of lead is as satisfactory as that depending upon the deposition of all the lead, as PbO_2, on the anode by the electrolysis of a nitric acid solution. The concentration of the nitric acid may be such that no copper will be deposited on the cathode, or more dilute nitric acid may be used and the copper determined simultaneously.

Procedure. — Transfer the neutral solution of lead nitrate, containing not more than 0.5 g lead, to a platinum dish whose inner surface is unpolished (as recommended by Classen), add 20–30 ml of 15 N pure nitric acid, dilute to 150–200 ml, and electrolyze in the cold with a current of about 0.5–1 ampere at 2–2.5 volts. When the electrolysis is carried out in the cold, all the lead will be deposited as the peroxide at the end of $2\frac{1}{2}$ or 3 hours. Only an hour or an hour and a half is required if the temperature of the cell is kept at 50°–60°. If it is desired to let the electrolysis run over night, a current of 0.05 ampere is sufficient.

A suitable arrangement of the electrolytic apparatus is shown in Fig. 42, but the dish should in this case serve as anode and the platinum

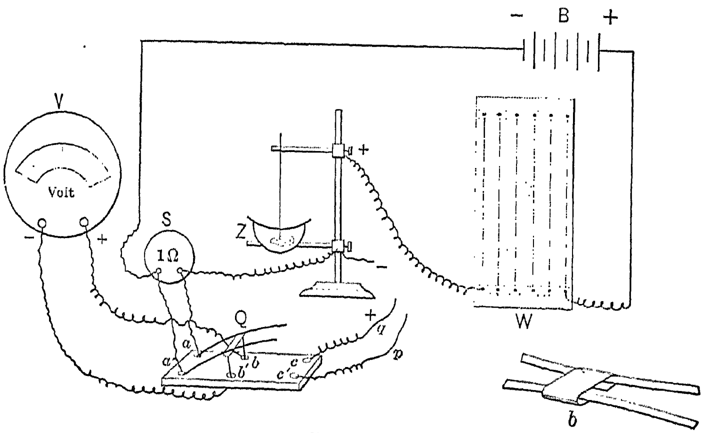

FIG. 42.

spiral as cathode, although the drawing is marked otherwise. The resistance W is made by taking about 10 m of nickel wire of about 0.5-mm diameter, fastening it to a board as shown in the drawing, and connecting the wires in pairs by means of a brass hook, of which only one is shown in the sketch. By suitably moving these hooks it is possible to

vary the resistance at will. Instead of this arrangement, any good rheostat may be used; such an apparatus is more convenient but also more expensive. At the end of the electrolysis, which is shown by the fact that dilution with a little water so as to expose a fresh surface of platinum causes no yellowish brown coating to appear at the end of half an hour, wash the dish without breaking the current. This is accomplished by introducing distilled water while the solution is being siphoned off. It is important in this operation to keep the deposit of lead peroxide completely covered with liquid. When the solution that is being siphoned off no longer reacts acid, or at least only barely acid, the washing is complete and the circuit can be broken. Finally wash the dish once more with distilled water, dry at 180°, and weigh. The results obtained are usually slightly high on account of the lead peroxide not being completely anhydrous when dried at this temperature. It is well, therefore, to heat the dish gently over the free flame before weighing, thereby readily converting the peroxide into lead oxide, PbO.*

Remark. — By employing a stronger current and keeping the solution warm during the electrolysis, the deposition is complete in much less time, but according to the author's experience the results obtained are not as satisfactory. By rotating one of the electrodes and using a stronger current, the deposition can be made to take place in a short time. The use of a gauze anode is not advisable with quantities of lead exceeding 0.1 g because the deposit does not adhere well and is likely to fall off on washing and on drying. When the gauze electrode is used, place the electrode in a small beaker so that any deposit that falls off during drying will be saved. If a little lead deposits on the cathode, this is remedied by stopping the current for a short time, toward the end of the electrolysis. To cleanse the electrode use a mixture of dilute nitric acid and some sodium nitrite.

Besides the above-mentioned forms, lead is also determined as the chromate (cf. p. 203) and sometimes as the chloride.

BISMUTH, Bi. At. Wt. 209.0

Forms: $BiPO_4$, $BiOCl$, Bi_2O_3, Bi_2S_3, Bi

1. Determination as Bismuth Phosphate, $BiPO_4$

It is generally agreed that the determination as phosphate is the most satisfactory method that has been proposed for determining bismuth.†

Treat the cold solution containing no chloride and not more than 0.5 g of Bi at a volume of not over 100 ml with strong ammonia until a

* Cf. W. C. May, *Z. analyt. Chem.*, **14**, 347 (1875).

† L. Moser, *Die Bestimmungsmethoden des Wismuths*, Stuttgart, 1909. W. R. Schoeller and E. F. Waterhouse. *Analyst*, **45**, 435 (1920).

slight permanent precipitate is obtained. Dissolve this in 2 ml of 6 N nitric acid. Heat to boiling, and to the boiling solution add, while stirring constantly, 10 per cent diammonium phosphate solution from a buret, using 20 ml for 0.05 g, 30 ml for 0.1 g, 40 ml for 0.2 g, and 60 ml for 0.4–0.5 g of Bi. When the required volume of phosphate has been added, dilute to 400 ml with boiling water and allow to stand 10–15 minutes on a hot plate or water-bath. Decant through a weighed Gooch crucible, and wash the precipitate with 3 per cent ammonium nitrate solution containing a few drops of nitric acid per liter. Dry, ignite gently inside another crucible, and weigh as $BiPO_4$.

Determination of Bismuth in Ores

Digest 1 g of the powdered sample with 15 ml of concentrated hydrochloric acid. Add concentrated nitric acid to dissolve any sulfide and evaporate nearly to dryness. Add 10 ml of nitric acid and again evaporate. Take up the residue in 15 ml of strong hydrochloric acid and dilute with water to about 50 ml. Filter off the silicious residue and wash with normal hydrochloric acid.

If lead is present, add 1–2 g of fine iron wire and heat at the boiling temperature for 10–20 minutes. If lead is absent omit this treatment and precipitate with hydrogen sulfide at once.

Filter off the metallic bismuth and excess iron, wash with hot water, and return to the original beaker. Dissolve in a little hot hydrochloric acid and a few drops of bromine. When all the bismuth has dissolved, boil off the excess bromine and dilute until the solution is about 0.3 N in hydrochloric acid. Saturate this solution with hydrogen sulfide, filter, and wash with very dilute acid containing hydrogen sulfide. Return the sulfide precipitate to the beaker, and treat with hot 2 N sodium hydroxide and hydrogen sulfide, adding some fresh sodium cyanide solution if copper is present. Filter through the same filter, and wash with hot, dilute sodium sulfide solution. Spread the filter against the side of a beaker and rinse off the precipitate of bismuth sulfide. Clean the paper with hot 6 N nitric acid and then discard it. Add more nitric acid to dissolve all the precipitate and evaporate the resulting bismuth nitrate solution until the sulfur has fused to a transparent globule. Do not use bromine at this stage or low results will be obtained. Filter off the sulfur through a small filter and precipitate the bismuth as phosphate by the procedure described above.

2. Determination of Bismuth as Basic Chloride, BiOCl

To the hydrochloric acid solution, which must not contain any phosphoric acid and preferably no sulfuric acid, add ammonia water until further addition will cause precipitation. Dilute with considerable water, stir, and allow the precipitate to settle. To the clear, supernatant solution add more water and repeat this treatment until further dilution causes no more precipitation. If nitric acid was present in the solution use dilute ammonium chloride solution instead of pure water. Filter, wash with hot water, dry at 105°, and weigh.

Remark. — This is one of the simplest methods for determining bismuth and is much used in practice. Antimony and tin must be absent.

3. Determination as Bismuth Oxide, Bi_2O_3

Solid bismuth nitrate or carbonate is readily changed to the oxide by gentle ignition. When bismuth, however, is present *in solution* as the nitrate, it should be first precipitated as the basic carbonate and this changed by ignition to the oxide.

Procedure. — Dilute the solution with water (if a turbidity ensues it makes no difference) so that not more than 0.1 g of metal is present in 150 ml, add a slight excess of ammonium carbonate solution, heat to boiling, and allow the precipitate to settle. Filter, wash the precipitate with hot water, dry, ignite,* and weigh as Bi_2O_3. If the solution from which the bismuth is to be precipitated contains besides nitric acid other acids (HCl, H_2SO_4, etc.), the precipitate produced by ammonium carbonate always contains basic salts which cannot be converted to the oxide by ignition.

4. Electrolytic Determination of Bismuth†

Dilute the solution of the nitrate to about 100 ml. Too much acid should not be present but just enough to prevent the formation of insoluble basic salt; not more than 2 ml of concentrated acid should be used. Heat to boiling and electrolyze with a gauze cathode and with the electrodes connected directly to the two poles of a 2-volt storage cell. The electrolysis requires 2–3 hours with 0.3 g of metal. Wash the electrode with water without interrupting the current, then remove it from the bath, wash with alcohol, dry by holding high above a flame, cool in a desiccator, and weigh.

COPPER, Cu. At. Wt. 63.57

Forms: CuO, Cu_2S, Cu, $Cu_2(CNS)_2$

1. Determination as Copper Oxide, CuO

The copper solution must be free from organic substances and ammonium salts. Heat it to boiling in a porcelain dish and add pure potassium hydroxide solution, drop by drop, until the precipitate be-

* If the precipitate is large in amount, place the greater part on a watch glass and dissolve the remainder that adheres to the filter in hot, dilute nitric acid. Evaporate the solution to dryness in a weighed platinum dish and add the main portion of the precipitate. Heat the dish and its contents at first gently but finally over the full flame of a Bunsen burner.

† O. Brunck, *Ber.*, **35**, 1871 (1912).

comes dark brown and is permanent, and the solution itself shows an alkaline reaction toward litmus paper. After the precipitate has settled, carefully pour off the upper liquid through a filter and wash the precipitate by decantation with hot water until the wash water no longer shows an alkaline reaction. Transfer the precipitate to the filter and continue washing with hot water. Usually a small amount of copper oxide adheres to the porcelain dish so firmly that it can be removed only by vigorous rubbing with a glass rod covered at the end with a piece of rubber tubing, and finally when the precipitate is removed from the dish some will then remain on the rubber. Consequently it is better to proceed as follows: Remove as much of the precipitate as possible by a stream of water from the wash-bottle, then add 2 drops of $6\,N$ acid, and, by inclining the dish and rubbing with the glass rod, moisten with the acid all the precipitate remaining on the dish. Two drops of the acid are sufficient, with correct manipulation, to dissolve all the copper oxide. Prepare a small fresh filter, and holding the dish in an inclined position, so that the liquid remains near its lip, wash the sides once with hot water and heat the contents of the dish (which is continually maintained in this inclined position) to boiling over a small flame; add dilute potassium hydroxide solution drop by drop until the copper is again precipitated. Avoid a large excess of alkali hydroxide on account of its solvent action upon the precipitate.* Quickly pour the contents of the dish through the small filter and immediately wash the dish once with water. All the copper oxide is now on the filter. Wash the precipitate with hot water, dry both filters, and transfer most of the precipitate to a porcelain crucible. Ignite the filters in a platinum spiral, and add the ash to the contents of the crucible. Cover the crucible, ignite at first gently, and finally with the full heat of the Bunsen burner; weigh as CuO. If the process is carried out carefully, the results obtained are almost the theoretical values but as a rule they are a trifle high.

Remark. — According to A. Bayer,† copper can be determined in the presence of all other metals of the hydrogen sulfide group in the following manner: Add caustic soda solution to the copper solution until the copper is all precipitated as hydroxide and then add enough Rochelle salt (sodium-potassium tartrate) to dissolve the precipitate. Heat to boiling in a porcelain dish and to the boiling solution add 2 ml of 5 per cent hydroxylamine hydrochloride. By boiling one minute all the copper (not more than 0.2 g should be present) is precipitated as cuprous oxide.

$$1\left\langle\begin{matrix} O\cdot CH\cdot CO_2Na \\ O\cdot CH\cdot CO_2K \end{matrix}\right. + 2\,NH_2OH + H_2O \rightarrow 2\,Cu_2O + 4\,KNaC_4H_4O_6 + N_2O$$

* Cf. Vol. I.

† *Z. anal. Chem.*, **1912**, 729.

Filter off the cuprous oxide into a Gooch crucible, wash with hot water, dry, ignite in the air, and weigh as CuO.

2. Determination as Cuprous Sulfide, Cu_2S

The copper solution may contain enough acid to make it 1.8 N with sulfuric acid but need not contain more than enough acid to make it 0.3 N to prevent the precipitation of metals of the ammonium sulfide group. Heat the solution to boiling, and introduce hydrogen sulfide until it becomes cold. If considerable acid was present, the precipitate settles quickly in large flocks and the upper liquid appears perfectly colorless. Before filtering, prepare the wash liquid by passing hydrogen sulfide through the long tube of a wash-bottle for one minute, then close the short tube with a piece of rubber tubing and shake vigorously. As soon as no more bubbles pass through the liquid, the water is saturated; this takes about a minute at the most.

Place a paper filter in a funnel containing a platinum cone or a small hardened filter and fit the funnel to a suction-bottle. Start filtering without using suction, taking care that the filter is constantly kept full. When all the precipitate is on the filter, wash the precipitate with hydrogen sulfide water containing 4 per cent of acetic acid, and, at this point also, the filter must be kept full of liquid. Continue washing until 1 ml of the filtrate shows no test for mineral acid.* Now for the first time allow the filter to drain completely, with the aid of gentle suction. Dry completely by heating in the drying closet at 90°–100° for at least an hour.

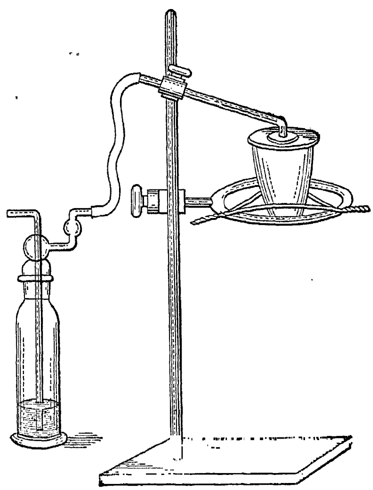

FIG. 43.

Transfer as much of the precipitate as possible to a weighed Rose crucible (of unglazed porcelain),† burn the filter in a platinum spiral, and allow the ash to fall at first upon an unglazed crucible cover, where it should be heated

* Test for sulfuric acid with barium chloride. To test for hydrochloric acid, boil the solution until the hydrogen sulfide is expelled and then treat with silver nitrate.

† A quartz crucible is more desirable, as the transformation of CuS into Cu_2S can then be watched.

gently till it glows, in order to make sure that it contains no unburned carbonaceous matter. Then add the ash to the main portion of the precipitate in the crucible. Also add a little sulfur that has been recrystallized from carbon bisulfide. Place the perforated cover on the crucible (Fig. 43), pass a stream of hydrogen through it (the wash-bottle shown contains concentrated sulfuric acid*), and heat the crucible at first over a small flame and finally so that the bottom of the crucible glows faintly. At this temperature the cupric sulfide is changed to cuprous sulfide, $2\,CuS = Cu_2S + S$.

Too strong heating is inadvisable, according to Hampe.†

When the excess of sulfur has been driven off (which can be readily ascertained by removing the cover of the crucible and finding no blue flame and no odor of burning sulfur), increase the current of hydrogen so that eight bubbles per second pass through the wash-bottle (at first, not more than four bubbles per second should have been the rate), and remove the flame. Allow the crucible to cool in the current of hydrogen and weigh after remaining in the desiccator for 15 minutes. The cuprous sulfide should be brownish black or black, and should show no reddish brown stains (due to Cu or Cu_2O); this is the case if the current of hydrogen was too slow during the cooling. To remedy this defect, add a little sulfur to the precipitate and repeat the heating in hydrogen.

Remark. — It is evident that the sulfur used for this experiment should leave on ignition no weighable residue. This is why the sulfur used should be recrystallized from carbon bisulfide.

The reason why it is necessary to keep the funnel filled with liquid during the filtration and washing of the cupric sulfide is this: If moist copper sulfide is exposed to the air it is quickly oxidized and the hydrogen sulfide wash water acts upon the salt formed by the oxidation ($CuS_2O_3 \cdot CuSO_4$), and transforms it into colloidal cupric sulfide, which passes through the filter, and on coming in contact with the acid filtrate is coagulated. If, however, the precipitate is not exposed to the air during the filtration there is no oxidation and the filtrate remains clear.

Instead of changing the cupric sulfide into cuprous sulfide, it has been proposed to convert it to oxide by ignition in the air and weigh the copper in this form. If, however, the highest degree of accuracy is desired, this should not be done, for the ignited product always contains some sulfate. When this method is chosen, the cupric sulfide should be heated in a glazed procelain crucible, at first over a small flame, so that the mass does not melt, and the heat gradually increased until finally a blast lamp is used and the copper weighed as CuO. The results are about 0.1 per cent

* If the hydrogen is prepared from zinc and hydrochloric acid, the gas should be passed first through water and then through a wash-bottle containing concentrated sulfuric acid.

† *Z. anal. Chem.*, **38**, 465 (1894).

too high when not more than 0.2 g of precipitate is present. Holthof* states that copper oxide absolutely free from sulfate can be obtained if the precipitate is ignited wet in an inclined porcelain crucible.

3. Determination as Cuprous Thiocyanate, $Cu_2(CNS)_2$ Method of Rivot†

The solution should be slightly acid with sulfuric or hydrochloric acid and contain 0.2 g or less of copper in 100 ml. Oxidizing agents must be absent. To the solution add an excess of sulfurous acid,‡ and normal ammonium thiocyanate solution, drop by drop with constant stirring, whereby at first a greenish mixture of cupric and cuprous salts is precipitated, which after stirring becomes pure white cuprous thiocyanate. Allow the precipitate to settle completely (this requires several hours). Then filter and wash with cold water until the filtrate shows only a slight reddish coloration when ferric chloride is added. Finally wash several times with 20 per cent alcohol, dry at 110°–120°, and weigh as $Cu_2(SCN)_2$. The cuprous thiocyanate can be dried at a temperature as high as 160°, but at 180° it begins to decompose. The Munroe crucible can be used to advantage in this determination. The precipitate permits rapid filtration, and a turbid filtrate is never obtained. After the determination is finished, the greater part of the precipitate can be shaken out of the crucible, and the remainder dissolved in hot nitric acid.

4. Electrolytic Determination of Copper

This most accurate and most convenient of all methods for the determination of copper was first proposed by W. Gibbs in 1864.§ Copper may be deposited by means of the electric current from acid, alkaline, and neutral solutions, but for analytical purposes only the use of acid solutions is of importance.

Procedure. — The safest way, according to F. Förster,|| is to deposit the copper from a sulfuric acid solution. To the neutral solution containing the copper in the form of sulfate, add 10 ml of 2 N sulfuric acid, dilute the solution to a volume of 100 ml, and electrolyze with exactly 2 volts potential at the electrodes by simply connecting the electrodes with the poles of a single storage cell. The electrolysis requires at least

* *Z. anal. Chem.*, **28**, 680 (1889).

† *Compt. rend.*, **38**, 868; see also R. G. van Name, *Z. anorg. Chem.*, **26**, 230, and Busse, *Z. anal. Chem.*, **17**, 53, and **30**, 122.

‡ Instead of sulfurous acid, ammonium bisulfite may be used, prepared by saturating aqueous ammonia with SO_2.

§ *Z. anal. Chem.*, **3**, 334 (1864).

|| *Z. angew. Chem.*, **1906**, 1842, 1849; **1907**, 812; *Ber.* **1906**, 1890.

8 hours if done at the ordinary temperature, but by keeping the solution at 70°–80°, 0.2 g of copper is deposited in 60–80 minutes. If, therefore, it is desired to carry on the electrolysis over night, it is done in the cold. It is very easy to decide when the electrolysis is finished by adding a little water and noticing whether there is any more copper deposited upon the freshly exposed electrode surface. Wash the cathode with water, without breaking the circuit, exactly as was described under the electrolytic determination of nickel (p. 143). Finally, rinse with alcohol, dry by holding it high above a flame, cool in a desiccator, and weigh.

If these directions are followed closely, the copper is never deposited in a spongy condition. The presence of Ni, Co, Fe, Zn, or Cd does not influence the analysis, and the copper may be separated from these elements by means of such an electrolysis.

If the solution to be analyzed contains nitric acid and some of the above-mentioned metals, evaporate to dryness, heat with a little sulfuric acid until dense fumes are evolved, cool, add 10 ml of 2 N sulfuric acid, dilute to 100 ml, and electrolyze as described above.

If only copper is present in the solution, however, it may be deposited satisfactorily in the following manner: To 100 ml of the neutral solution add 4–5 ml of concentrated nitric acid. If, originally, it contained more nitric acid than this, either evaporate to dryness or neutralize with ammonia, and then add the required quantity of nitric acid. Boil gently to remove nitrous fumes. Rinse off the cover glass and wash down the sides of the beaker. Add 0.1 g of solid urea, to react with any remaining nitrous acid, and electrolyze at 50°–60° with a current of 1 ampere and electrode potential of 2–2.5 volts, using a gauze cathode. The electrolysis is over at the end of 2 hours, when not more than 0.3 g of copper is present. Finish the analysis as above, but there is more danger of traces of copper being dissolved while the electrodes are being removed. If the electrolysis is continued too long, some nitrous acid is formed and the deposit begins to dissolve. To remedy this, add a little more urea and electrolyze a little longer.

The best way to test the solution to see if all copper is removed is to clean the electrodes and see if any gain in weight is experienced by further electrolysis with the cleaned electrodes.

Remark. — The copper may be deposited electrolytically much more rapidly by the use of a rotating electrode, or any stirring arrangement and a stronger current. The use of a gauze cathode also permits a higher amperage. The solution should not be diluted too much, as spongy deposits are obtained from very dilute solutions unless a very weak current is used. As a general rule, the more concentrated the copper solution, the stronger the current that can be used.

CADMIUM, Cd. At. Wt. 112.4

Forms: Cd, $CdSO_4$, CdO and $Cd_2P_2O_7$

1. Electrolytic Determination of Cadmium

Of all the methods for the determination of cadmium the electrolytic method is not only the most convenient, but by far the most accurate, and of the many methods proposed that of Beilstein and Jawein* can be recommended. To the solution of the sulfate, add a drop of phenolphthalein indicator solution, and then pure sodium hydroxide solution until a permanent red color is obtained. Now add 10 per cent pure potassium cyanide solution with constant stirring, until the precipitate of cadmium hydroxide produced by the caustic soda has completely dissolved; an excess of potassium cyanide should be scrupulously avoided. Dilute the solution with water to 100–150 ml and electrolyze in the cold, using a gauze cathode. From 5–6 hours are required with a current of 0.5–0.7 ampere and an electromotive force of 4.8–5 volts; at the end of this time increase the current to 1–1.2 amperes and electrolyze the solution for 1 hour more. If these directions are followed, all the cadmium (if not more than 0.5 g is present) will be deposited as a firmly adhering, dull deposit of nearly silver-white metal. Stop the current, quickly pour off the liquid, and wash the deposited metal first with water, then with alcohol, and finally with ether. Dry in the usual way and weigh.

After the electrolysis is finished, the solution should always be tested for cadmium. For this purpose, saturate it with hydrogen sulfide. If much cadmium is present, a yellow precipitate is obtained, but if very little, a yellow coloration results. This color is due to the formation of colloidal cadmium sulfide, and it is so intense that R. Philipp estimates the quantity of cadmium not precipitated by comparing the shade with that produced in a solution containing a known quantity of cadmium and the same amounts of potassium cyanide and caustic potash as in the solution tested.

Remark. — If for the electrolysis a current of 0.5 ampere is used, not all the cadmium will be deposited at the end of 12 hours; if the current is increased at the end, as above stated, to 1 ampere, however, the electrolysis will surely be finished in 6 or 7 hours. To work with the stronger current from the beginning is not to be recommended unless a gauze cathode is used, or one of the electrodes is rotated, for otherwise the metal is deposited in a spongy form and on washing some of it is likely to be lost.

A solution containing 0.4568 g Cd., 3 g KCN, 1 g NaOH, and diluted to 125 ml

* *Ber.*, **12**, 446.

with water, can be electrolyzed in 15 minutes with a current of 5 amperes and 5.5 volts if one of the electrodes is rotated.

From neutral and weakly acid solutions, cadmium can be deposited electrolytically, but not from strongly acid solutions.

2. Determination as Cadmium Sulfate, $CdSO_4$

Next to the electrolytic method, the determination of cadmium as sulfate is the best. If the cadmium is combined with a volatile acid, treat the compound in a weighed porcelain crucible with a slight excess of dilute sulfuric acid, evaporate the solution on the water-bath as far as possible, and finally remove the excess of sulfuric acid by heating in an air-bath (see Fig. 14, p. 37). Apply the heat at first slowly, and raise the temperature gradually until finally no more fumes of sulfuric acid are evolved. The outer crucible can even be heated with the full flame of a Teclu burner without running any risk of decomposing the cadmium sulfate; however, it is not necessary to heat it so strongly. As soon as the fumes of sulfuric acid cease to come off, stop heating and weigh the crucible and its contents after cooling in a desiccator. The cadmium sulfate should be pure white and should dissolve in water to form an absolutely clear solution.

If the cadmium has been precipitated from a solution as the sulfide, place the greater part of the precipitate in a large porcelain crucible, cover with a watch glass, and treat with $3\,N$ hydrochloric acid on the water-bath. After the precipitate has dissolved and the evolution of hydrogen sulfide has ceased, wash the lower side of the watch glass, place the crucible under the funnel, and dissolve the precipitate which adhered to the filter paper by dropping hot, $3\,N$ hydrochloric acid upon it. Finally wash the filter with hot water and evaporate the solution upon the water-bath, continuing as described above.

The Precipitation of Cadmium as Sulfide

The frequently recommended determination of cadmium as the sulfide must be rejected; it is inaccurate. It is not possible to precipitate pure cadmium sulfide from acid solutions by means of hydrogen sulfide; the precipitate is always contaminated with a basic salt (Cd_2Cl_2S – Cd_2SO_4S, etc.), whether the precipitation takes place in cold or hot solutions, whether under atmospheric pressure or under increased pressure (in a pressure-flask), and in fact the amount of basic salt formed increases with the amount of free acid present. Results are obtained as much as 5 per cent too high. Follenius* attempted to make the method

* *Z. anal. Chem.*, **13**, 422.

possible by igniting an aliquot part of the dried and weighed precipitate in a stream of hydrogen sulfide. If the sulfide was contaminated with sulfate, he succeeded in changing it all to sulfide and obtained results that were acceptable. If, however, chloride was present, a considerable part was lost by sublimation, so that the results obtained were too low. Furthermore, it is not possible to ignite the cadmium sulfide with sulfur in a current of hydrogen, as was described under Zinc and Copper, for cadmium sulfide is so volatile that some of it is lost.

On the other hand, the method of precipitating the cadmium as sulfide from solutions containing 2 ml of concentrated sulfuric acid in 100 ml is to be recommended, for by this means a precipitate is obtained which can be readily filtered and which by solution in hot $6N$ hydrochloric acid and evaporation with sulfuric acid can be changed without loss to the sulfate and weighed as such.

3. Determination as Cadmium Oxide, CdO

Cadmium carbonate and cadmium nitrate can be changed to the oxide by strong ignition.

To the dilute, boiling cadmium solution add a slight excess of potassium carbonate, and when the precipitate has completely settled after standing for some time on the water-bath, filter it off, wash with hot water, and dry. Transfer as much of the dried precipitate as possible to a watch glass and set aside for the time being. Wash the filter with hot $2N$ nitric acid to dissolve the precipitate which still adheres to it, and receive the solution in a weighed porcelain crucible. Evaporate to dryness, add the main portion of the precipitate, and heat the crucible at first very gently until the whole mass has become a uniform brown. Now gradually raise the temperature until finally the full heat of the burner is reached. It is important during this operation to take care that the inner flame mantle does not touch the crucible, for otherwise reducing gases may enter and reduce a part of the oxide to metallic cadmium, which is volatile at this temperature.* The cadmium oxide is obtained as a brown powder which is infusible, insoluble in water, but readily soluble in dilute acids.†

Remark. — It is not advisable to precipitate the cadmium by means of *sodium* carbonate solution, for in that case it is difficult to wash the precipitate free from alkali.

* If the cadmium carbonate is filtered into a Munroe crucible, and ignited in an electric oven, the transformation takes place readily without danger of any volatilization.

† The oxide after ignition is a black, crystalline powder.

4. Determination of Cadmium as Cadmium Pyrophosphate*

The cadmium solution used for this method of analysis should not contain ammonium salt other than the reagent and should be faintly acid. If considerable acid is present, neutralize with sodium carbonate solution.

To the cold, faintly acid solution containing not over 0.2 g of cadmium in 100 ml, add a concentrated aqueous solution of $(NH_4)_2HPO_4$ until the weight of added salt is 10–15 times as great as that of the cadmium present. Allow to stand for 12 hours to allow the amorphous precipitate to become crystalline. Filter through a Gooch or Munroe crucible, wash with cold 1 per cent ammonium phosphate solution and finally with 60 per cent alcohol. Heat in an electric oven at 800°–900° and weigh as $Cd_2P_2O_7$.

SEPARATION OF THE SULFO-BASES FROM THE METALS OF THE PRECEDING GROUPS

Hydrogen sulfide added to a solution which is $0.3\,N$ in acid precipitates only the metals of the "hydrogen sulfide group." It is to be noted that zinc precipitates with this group if the solution is not acid enough, while if the solution is too acid lead and cadmium are often incompletely precipitated.

Analysis of Brass (Alloy of Copper and Zinc sometimes containing Small Amounts of Tin, Lead, Iron, and Nickel)

Weigh out 0.4–0.5 g of the alloy into a 200-ml casserole† and dissolve in 20 ml of $6\,N$ nitric acid. Cover the casserole with a watch glass to prevent loss by spattering. After the reaction begins to slacken, heat on the water-bath until all the metal is dissolved. Evaporate the solution just to dryness, moisten the residue with a little nitric acid, dissolve in about 50 ml of hot water, and if any metastannic acid settles out on standing filter it off, wash with hot water, dry, and determine the tin according to p. 224. To the cold filtrate add 3 ml of pure, concentrated sulfuric acid, evaporate the solution on the water-bath as far as possible, and then heat cautiously over a free flame until dense white fumes of sulfuric acid are evolved. Cool, treat the residue with 50 ml of water and 15 ml of alcohol, stir well, filter, wash, and determine the

* Miller and Page, *Z. anorg. Chem.*, **28**, 233 (1901).

† The borings are often somewhat oily. They should then be washed with ether before weighing. Cf. p. 230, footnote.

lead sulfate according to p. 186. Evaporate the filtrate until the alcohol is completely removed, dilute with 100 ml of water, heat the solution to boiling, and conduct hydrogen sulfide into it until it becomes cold. Then filter off the copper sulfide, wash first with hydrogen sulfide water containing, in every 100 ml, 20 ml of 2 N sulfuric acid, and at the end with 5 per cent acetic acid, also saturated with hydrogen sulfide, until the filtrate gives no precipitate on being treated with barium chloride. Determine the copper, according to p. 193, as Cu_2S.

Evaporate the filtrate from the copper sulfide to a small volume in order to remove the excess of hydrogen sulfide, oxidize the iron by the addition of bromine water, precipitate by ammonia, and filter. To make sure that the precipitate of ferric hydroxide contains no zinc, redissolve it in a little hydrochloric acid and repeat the precipitation with ammonia. Filter, wash, ignite and weigh as ferric oxide (cf. p. 99).

Make the combined filtrates from the ferric hydroxide acid with a little sulfuric acid, heat to about 50° C, and determine the zinc as zinc sulfide according to the "salting-out" method described on p. 168. For the determination of nickel, boil the filtrate from the zinc sulfide to expel the hydrogen sulfide and precipitate the nickel as the salt of dimethylglyoxime according to p. 140.

Determination of Copper, Lead, and Zinc in Brass

The best brass alloys contain very little tin, lead, iron, or nickel. In commercial laboratories, often the copper and lead contents are determined electrolytically and the zinc is determined *by difference*, that is, by subtracting the percentages of copper and lead from 100 per cent.

The following method of analysis, however, provides for the determination of copper, lead, tin, iron, and zinc and is capable of giving accurate results.

Weigh 0.9–1.0 g of the alloy into a slender beaker of about 150-ml capacity. Add 12 to 15 ml of 6 N nitric acid, cover the beaker, and heat gently till all the brass is dissolved. If a clear solution is obtained, no tin is present, and the solution after dilution is ready for electrolysis.

If a white precipitate of metastannic acid forms, evaporate the solution just to dryness but do not bake the residue. Add 2 ml of 6 N nitric acid, dilute with 25 ml of water, and boil gently to dissolve the nitrates of copper and zinc. Filter off the metastannic acid, wash it with hot water, ignite in a porcelain crucible, and weigh as SnO_2.

Dilute the clear solution of the nitrates to 100 ml and boil gently for 1 minute to remove any nitrous oxides. Wash down the sides of the beaker and the cover glass, and electrolyze with a current of 1–2 amperes using a gauze cathode and a rotating anode. After the solution has become colorless, continue the electrolysis 10 minutes longer, adding

1 g of urea and washing down the sides of the beaker. The electrolysis ought not to require more than 1 hour at the most. A suitable apparatus is shown in Fig. 38, p. 142.

Wash the electrodes while lowering the beaker and while the current is still flowing. Dip them in alcohol and dry a very short time in the hot closet at 105°. The deposit on the cathode is pure copper, and that on the anode is lead dioxide, PbO_2.

To make sure that all the copper has been deposited, add a slight excess of ammonia to the entire solution. If a blue color is noticeable,* make acid with dilute sulfuric acid and electrolyze with clean electrodes until all the copper is removed.

Test for Iron and Aluminum

To the electrolyzed solution add a little bromine water, to make sure that any iron is in the ferric condition, and enough ammonia to dissolve the zinc hydroxide precipitate that may form at the neutral point. If any precipitate of ferric or aluminum hydroxide forms, filter it off. To make sure that no zinc hydroxide is in the precipitate, redissolve the precipitate in a little hot $2N$ hydrochloric acid, dilute to 50 ml, and precipitate again by adding ammonia. Ignite and weigh the precipitate as Fe_2O_3. If there is any likelihood of aluminum being present, examine the ignited oxides as described on p. 114.

To the ammoniacal solution containing the zinc, add methyl orange indicator and enough hydrochloric acid to make the solution barely acid. Precipitate the zinc as phosphate, and finish the analysis as described on p. 147.

Often so little lead is present that a larger sample is desirable. When the lead alone is desired it is better to electrolyze in the presence of more concentrated nitric acid. Fischer and Schleicher† recommend the following procedure.

Electrolytic Determination of Small Quantities of Lead in Brass

Weigh out 3–4 g of brass into a 200-ml beaker and dissolve in 30 ml of $7.5\,N$ HNO_3. Dilute with 50 ml of water and heat till nitrous fumes are expelled. Add 8 ml of concentrated nitric acid and electrolyze at a volume of 85 ml with a current of 3 amperes at 60°. After 10 minutes all the lead will be deposited as PbO_2 on the anode. Then, without removing the anode, dilute to 130–140 ml and electrolyze an hour longer at 20–30° with a current of 3–4 amperes. It is best to add 1 g of urea

* A pale blue color may indicate the presence of nickel but usually is caused in brass analysis by a little copper which has escaped deposition.

† *Elektroanalytische Schnellmethode.*

at the beginning and end of this last period as otherwise nitrous acid may cause the lead dioxide precipitate to dissolve.

For determining small quantities of lead in brass or metallic copper the following procedure is excellent.

Determination of Lead in Brass as Chromate

Treat 5 g of the metal with 50 ml of 6 N nitric acid, and to the resulting solution add carefully 5 ml of concentrated sulfuric acid. Evaporate until heavy white fumes of sulfuric acid are evolved, cool, and carefully dilute with 100 ml of water. Boil until the sulfates of copper and zinc have dissolved, cool, and let stand at least 1 hour. Filter off the lead sulfate precipitate and wash it with cold, 2 N sulfuric acid until free from copper and then twice with cold water.

Dissolve the lead sulfate precipitate by treating it with a little hot ammonium acetate solution, prepared by making 6 N ammonium hydroxide solution slightly acid with 6 N acetic acid. Pour about 5 ml of the hot acetate on the filter, allow it to run through and then wash with a stream of hot water from the wash-bottle. Repeat the treatment, using 3 ml of acetate, and continue in this way until a little of the washings gives no black precipitate when added to dilute ammonium sulfide solution. Usually the entire precipitate will dissolve in 10 ml of ammonium acetate solution.

To the hot acetate solution add a slight excess of 10 per cent potassium dichromate solution. Heat till the precipitated $PbCrO_4$ has a good yellow color, filter into a Gooch crucible, wash with hot water, then with dilute alcohol, dry at 110°, and weigh as $PbCrO_4$.*

Determination of Copper in Iron and Steel

Dissolve 10 g of sample in 200 ml of 10 per cent sulfuric acid and when the metal is dissolved dilute to at least 500 ml with water. Heat to boiling and saturate with hydrogen sulfide. Filter on paper or paper pulp and wash a few times with a 1 per cent sulfuric acid solution saturated with hydrogen sulfide. Ignite the residue and paper in a porcelain crucible and fuse with a small amount of alkali pyrosulfate. Dissolve the cooled melt in the crucible in 1 to 2 ml of hydrochloric acid and a few milliliters of water, add 5 per cent sodium hydroxide (free

* The precipitate does not correspond exactly to the formula. The American Society for Testing Materials recommends the use of the factor 0.6375 instead of the theoretical 0.6410, but such a correction is unnecessary in the analysis of brass. The $PbCrO_4$ precipitate can be dissolved in 25 ml of hot 6 N sulfuric acid, and the chromium determined iodometrically, adding 1 g of KI, waiting 5 minutes and then titrating slowly with standard thiosulfate solution.

from organic matter) in slight excess, boil, digest, and filter. Dissolve the precipitate in hot dilute nitric acid, add 5 ml of concentrated sulfuric acid, evaporate to fumes of sulfuric acid, cool, dilute to 40 ml, and add 10 ml of concentrated ammonium hydroxide (*d.* 0.90). Heat the still acid solution to boiling and saturate with hydrogen sulfide. Filter, wash thoroughly with slightly acidified hydrogen sulfide water, ignite, and weigh as cupric oxide.

Remark. — This separates Cu from Mo and As, the only other members of the hydrogen sulfide group likely to be present.

SEPARATION OF THE SULFO-BASES FROM ONE ANOTHER

1. Separation of Mercury from Lead, Bismuth, Copper, and Cadmium

Method of Gerhard v. Rath

Principle. — This separation is based upon the insolubility of mercuric sulfide in boiling, dilute nitric acid (*d.* 1.2–1.3) and the solubility of the remaining sulfides in this acid.

Procedure. — The solution must contain the mercury entirely in the mercuric form and should be 0.3 N in hydrochloric or sulfuric acid. Into the hot, fairly dilute solution introduce hydrogen sulfide in excess. Filter off the precipitate, wash it with hydrogen sulfide water, transfer to a porcelain dish, and boil for a considerable length of time with nitric acid of the above concentration. Then dilute with a little water and wash with water containing nitric acid. The residue of mercuric sulfide thus obtained always contains sulfur, and if considerable lead was present it will also contain lead sulfate. Dissolve it, therefore, in a little aqua regia, dilute with water, filter from the separated sulfur and lead sulfate, and precipitate the mercury with ammonium sulfide (cf. p. 181) according to the method of Volhard. If some of the lead sulfate should go into solution with the mercury on treating with aqua regia, it will be converted by the ammonium sulfide and potassium hydroxide into insoluble lead sulfide, while the mercury will be in the form of its soluble sulfo-salt. In this case filter off the lead sulfide, wash with dilute potassium hydroxide solution, and precipitate the mercury as sulfide, as described on p. 181.

2. Separation of Bismuth from Lead

(*a*) *Method of Löwe**

Principle. — Bismuth nitrate is changed by the action of water into an insoluble basic salt, but lead nitrate undergoes no such transformation.

* *J. prakt. Chem.*, **74**, 345 (1858). Cf. Little and Cahen, *Analyst*, **35**, 301.

Procedure. — Evaporate the nitric acid solution of these two metals on the water-bath until it reaches a sirupy consistency. Add water, and after thorough stirring with a glass rod repeat the evaporation and continue this treatment until the addition of the water fails to produce any further turbidity, a sign that the bismuth has been completely converted into the basic salt $Bi_2O_2NO_3OH$. Add 100 ml of a cold 2 per cent ammonium nitrate solution, and after standing some time, with frequent stirring, to make sure that the lead nitrate is completely dissolved, filter the solution. Wash the precipitate with the dilute ammonium nitrate solution and dry. Transfer as much of it as possible to a weighed porcelain crucible, burn the filter and add the ash to the crucible, and ignite to a constant weight of Bi_2O_3.

From the filtrate precipitate the lead as sulfate, according to p. 185, and weigh as such. It is less satisfactory to precipitate the lead as sulfide and weigh it in this form after gentle heating with sulfur in a Rose crucible.

(*b*) *Method of Ledoux**

To 100 ml of the dilute nitric acid solution, add 6 N NH_4OH dropwise from a buret until a faint opalescence appears. Then add 1 cc. of 3 N HCl, dilute to 300 ml, and heat just to boiling. Allow to stand on the steam-bath for 2 hours or in a warm place over night. Filter off the precipitate of BiOCl and possibly SbOCl and a little $PbCl_2$, and wash the precipitate twice with boiling water. Dissolve it in a little 3 N HCl, and to the solution add an amount of water about 30 times as large as the amount of the acid used. If a precipitate appears on dilution, pay no attention to it. Saturate with hydrogen sulfide and filter off the Bi_2S_3 precipitate, which may contain Sb_2S_3 and a little PbS. Wash this precipitate once with water, twice with hot, diluted ammonium sulfide reagent to remove antimony, and then with more water. Dissolve the precipitate in a little hot 3 N HNO_3, washing the filter paper with this acid and finally with hot water. Dilute and reprecipitate the BiOCl exactly as described above. Dry at 100°, and weigh as BiOCl.

3. Separation of Bismuth from Copper

To the dilute solution add an excess of ammonium carbonate solution, heat gently, and filter. The precipitate of basic bismuth carbonate almost always contains small quantities of copper; redissolve it in nitric acid and repeat the separation by means of ammonium carbonate.

* A. H. Low, *Technical Methods of Ore Analysis*, Hillebrand-Lundell, *Applied Inorganic Analysis.*

Fuse the basic bismuth salt with potassium cyanide, leach the melt with hot water and weigh the residual bismuth.

For the copper determination, combine the two filtrates, evaporate to remove the excess of ammonium carbonate, make acid with sulfuric acid, and precipitate the copper by means of hydrogen sulfide. Weigh the copper as cuprous sulfide according to p. 193, or electrolyze the sulfuric acid solution as described on p. 195.

According to Fresenius and Haidlin, bismuth can be separated from copper very satisfactorily by means of potassium cyanide. For this purpose, treat the acid solution with a slight excess of sodium carbonate, add potassium cyanide, heat the solution, and filter. All the copper is found in the filtrate, while the precipitate contains bismuth oxide contaminated with alkali. Dissolve the residue, therefore, in nitric acid, precipitate the bismuth by means of ammonium phosphate, and determine as phosphate according to p. 189. Evaporate the filtrate containing the copper with nitric acid, to destroy the cyanide, and determine copper electrolytically according to p. 195.

Another method of carrying out the separation of bismuth from copper by means of KCN is to heat a mixture of the freshly precipitated sulfides with a solution of 3 to 4 g of KCN in a little water. Bi_2S_3 remains undissolved.*

4. Separation of Lead from Copper by Means of Electrolysis

This separation depends upon the fact that the electric current deposits lead quantitatively as PbO_2 upon the anode from solutions containing considerable nitric acid, while the copper is either not deposited at all under these conditions or is found upon the cathode to some extent. After the lead is completely deposited, the copper solution is poured into a second weighed platinum dish, the excess of the acid is neutralized with ammonia, and the solution again electrolyzed. The copper will now deposit quantitatively upon the cathode.

Procedure. — Transfer the solution of the two nitrates to a platinum dish of the form recommended by Classen with the inner surface unpolished. Add 15 ml of 15 N nitric acid to 150 ml of solution and electrolyze at 50°–60° C with a current of 1–1.5 amperes and an electrode potential of 1.4 volts. After 1–1.5 hours practically all the lead will be deposited upon the anode (dish) in the form of a firmly adhering brown coating of lead peroxide, PbO_2. At the cathode (a plate electrode) a considerable part of the copper will be deposited, but the remainder will still be in solution. Break the circuit, and pour the solution as quickly as possible into a second weighed platinum dish, adding the washings

* A. H. Low, *Technical Methods of Ore Analysis.*

to this dish. After washing the electrodes with water, dry the first dish with the PbO_2 deposit at 180°, and weigh. The solution in the second dish contains a little lead and some copper. Make it slightly ammoniacal, add 4 ml of 15 N nitric acid, and electrolyze the solution at 60°. The platinum dish now serves as the cathode, while the plate electrode* serves as the anode; if traces of lead remain in solution after the first electrolysis, it will now be deposited. After an hour or two with a current of 1 ampere all the remaining copper and lead will be deposited. When the electrolysis is complete, wash the electrodes without breaking the circuit and determine the weight of the copper and PbO_2.

If only a little lead is present it is better to carry out the electrolysis as described on p. 201 or 202.

5. Separation of Lead from Copper and Cadmium

(From Bismuth Less Satisfactorily)

To the solution of the nitrates or chlorides add an excess of sulfuric acid, evaporate to remove the nitric or hydrochloric acid, and determine the lead as sulfate as described on p. 185.

6. Separation of Copper from Cadmium

(*a*) *By Electrolysis*

The solution should contain not more than 0.2 g of cadmium. To the neutral solution add 10 ml of 6 N nitric acid, dilute to 150 ml in a platinum dish, and electrolyze with the dish as cathode. Adjust the anode, a disk electrode, so that it dips into the liquid only a short way. Under these conditions, 0.2 g of copper is deposited, perfectly free from cadmium, within 12–14 hours by a current of 0.2–0.3 ampere and a voltage of 1.9–2.3 volts. With a current of 1–1.5 amperes and 2.5–2.6 volts electrode potential, the copper is deposited in about 5 hours. When the deposition is complete, siphon off the solution while pouring pure water into the dish without breaking the current. Finally rinse the dish with alcohol, dry, and weigh with the deposited copper. Add a little sulfuric acid to the solution, evaporate to expel the nitric acid, cool, dilute, and electrolyze the cadmium from cyanide solution as described on p. 197.

Remark. — If considerably more than 0.2 g Cd is present in 150 ml of the solution, there is danger of small amounts of cadmium separating out upon the copper during the washing of the deposit, especially if the anode extends well into the

* The plate electrode with copper upon it was weighed, cleaned, and then weighed again.

solution. This is because the concentration of the acid becomes less during the washing. In analyzing a solution containing a large amount of cadmium and small amount of copper, therefore, it is best to wash at first with 2 per cent nitric acid rather than with distilled water.

The separation requires but a few minutes with a rotating anode or cathode, and a stronger current.

F. Foerster recommends the following conditions for an electrolytic separation of copper and cadmium: Electrolyte: 100 ml of 2 N sulfuric acid. Electrodes: a large platinum gauze electrode as cathode and a smaller one as anode. Connect the electrodes directly with the terminals of a single storage cell so that the voltage is kept constant throughout the electrolysis. After 60–90 minutes 0.2 g of copper will be deposited completely. Remove the cathode in the usual way (p. 143), neutralize the solution with potassium hydroxide solution, add potassium cyanide, and electrolyze for cadmium according to directions on p. 197.

(b) *Method of Rivot-Rose*

Precipitate the copper as thiocyanate according to p. 195, and in the filtrate precipitate cadmium as sulfide and determine as sulfate according to p. 198. The results are good.

B. DIVISION OF THE SULFO-ACIDS

Arsenic, Antimony, Tin

(SELENIUM, TELLURIUM, GOLD, PLATINUM, TUNGSTEN, MOLYBDENUM, VANADIUM)

ARSENIC, As. At. Wt. 74.96

Forms: As_2S_3, As_2S_5, $Mg_2As_2O_7$

The three best ways of determining arsenic are (1) the gravimetric determination as As_2S_3 (see below); (2) the volumetric determination of the silver in a precipitate of Ag_3AsO_4 (see Method of Low-Pearce-Bennett); and (3) the iodometric titration of trivalent arsenic in a buffered solution (see Iodometry).

1. Determination as Arsenic Trisulfide, As_2S_3

For the determination of arsenic in this form, it must be present in its trivalent state, *i.e.*, as arsenious acid or as arsenite.

Make the solution strongly acid with hydrochloric acid and precipitate the arsenic in the cold with hydrogen sulfide. Remove the excess of the latter by a stream of carbon dioxide, and filter through a Gooch crucible that has been previously dried at 105°. Wash the precipitate with hot water, dry at 105° to constant weight, and weigh as As_2S_3.

2. Determination as Arsenic Pentasulfide, As_2S_5, according to Bunsen*

Modified by Fr. Neher†

To the solution, which must contain all the arsenic as arsenic acid, add 12 *N* hydrochloric acid little by little (it is best to keep the solution cooled by surrounding the flask with ice) until the solution is at least 4 *N* in hydrochloric acid. Conduct a very rapid stream of hydrogen sulfide into this solution (contained in a large Erlenmeyer flask) until it is saturated with the gas. Then stopper the flask and allow to stand 2 hours. Filter off the arsenic pentasulfide through a Gooch crucible which has been dried at 105°, and wash the precipitate thoroughly with water, then with hot alcohol (to hasten the subsequent drying). After drying at 105° weigh the precipitate as As_2S_5. It is not necessary to wash it with carbon bisulfide.

Remark. — If the above directions are followed exactly, this method gives faultless results. If, on the other hand, the directions are deviated from in the slightest respect, the precipitate is likely to contain some arsenic trisulfide, whereby low results will be obtained. If the solution is not kept cool and the hydrochloric acid is added too rapidly, the heat of the reaction suffices to change a part of the arsenic pentachloride (this compound probably exists in solution) to arsenious chloride and chlorine, so that on passing hydrogen sulfide into the solution a mixture of arsenic trisulfide and arsenic pentasulfide will be obtained.

3. Determination of Arsenic as Magnesium Pyroarsenate, according to Levol

The solution must contain all of the arsenic as arsenate, and have a volume of not more than 100 ml per 0.1 g arsenic. Add 5 ml of 12 *N* hydrochloric acid drop by drop, with constant stirring, and then, for each 0.1 g of arsenic, add 7–10 ml of magnesia mixture‡ and a drop of phenolphthalein indicator solution. Now, with constant stirring, add 6 *N* ammonia from a buret until the phenolphthalein imparts a permanent red color to the solution, and then add enough more ammonia to make one-third the volume of the neutralized solution. After standing 12 hours filter the liquid through a Gooch or Munroe crucible. Transfer the precipitate in the beaker to the crucible by some of the original solution blown from a small wash-bottle. Wash the precipitate with 1.5 *N* ammonia solution containing 2–3 per cent of ammonium

* *Ann. Chem. Pharm.*, **192**, 305.

† *Z. anal. Chem.*, **32**, 45; see also Brunner and Tomicek, *Monatsh.*, 8, 607; McCay, *Z. anal. Chem.*, **27**, 682, and J. Thiele, *Ann. Chem. Pharm.*, **265**, 65.

‡ Dissolve 55 g crystallized magnesium chloride and 70 g ammonium chloride in 650 ml water and dilute to a volume of 1 l with ammonia water, *d.* 0.96.

nitrate until free from chloride. Drain the crucible as completely as possible by suction, dry at 100°, and heat in an electric oven quite gradually to a temperature of 400° to 500°, until no more ammonia is evolved. Then raise the temperature to 800°–900° and keep there for about 10 minutes. Cool the crucible in a desiccator and weigh as $Mg_2As_2O_7$.

If an electric oven is not available, place the crucible with the precipitate in an air-bath (cf. Fig. 14, p. 37), having the bottom of the outer Gooch crucible come within about 2–3 mm of the bottom of the crucible. Sprinkle a thin layer of powdered ammonium nitrate* upon the precipitate, and heat, gently at first, gradually increasing the temperature until the outer crucible is light red. Cool in a desiccator and weigh as $Mg_2As_2O_7$. The results obtained are excellent.

Remarks. — The precipitate produced by the magnesia mixture has the formula $MgNH_4AsO_4{\cdot}6H_2O$ and loses $5\frac{1}{2}$ molecules of water at 102°; it has, therefore, been proposed to weigh the precipitate after drying at this temperature, but it is impossible to obtain a constant weight. According to Levol, 600 ml of pure water dissolve 1 g of magnesium ammonium arsenate, but J. F. Virgili† found that it required 25 l of 1.5 *N* ammonia to dissolve 1 g of the precipitate. A precipitate of As_2S_3 or of As_2S_5 can be analyzed by the above method after treating the precipitate with HCl and $KClO_3$ as in qualitative analysis.

Colorimetric Determination of Arsenic

Small quantities of arsenic, such as are present in wall papers, may be estimated very accurately by means of the Marsh apparatus, comparing the mirror with a series of standards formed with known quantities of arsenic.‡ It is just as accurate, however, to use the much simpler apparatus recommended for the Gutzeit test. Treadwell and Comment§ allow the arsine to react with disks containing silver nitrate and compare the resulting color with a standard which, unfortunately, must be produced freshly with each analysis, as it does not keep very well. Almost equally accurate and much more convenient are the method of F. Hefti|| and that of C. R. Sanger and O. F. Black¶ in which the arsine is made to react with mercuric chloride paper.

* Instead of using ammonium nitrate, the crucible may be provided with a perforated cover and heated in a current of oxygen.

† *Z. anal. Chem.*, **44**, 504 (1905).

‡ C. R. Sanger, *Am. Chem. J.*, **13**, 431 (1891); *Z. anal. Chem.*, **38**, 137 and 377; G. Lockemann, *Z. angew. Chem.*, **1905**, 429 and 491.

§ This method was given in the early editions of this book.

|| *Inaug. Dissert.* Zürich, 1907.

¶ *Proc. Am. Acad. Arts and Sci.*, No. 8, 1907; *J. Soc. Chem. Ind.*, **26**, 1115 (1907).

(*a*) Method of Hefti

First destroy all organic matter by heating the sample in a tube (see Vol. I), with fuming sulfuric and nitric acids, both of which must be free from arsenic. Evaporate the resulting liquid with sulfurous acid on the water-bath to reduce the arsenic acid to arsenious acid.* When all the excess of SO_2 has been expelled, pour the solution into the graduated tube *T* of the apparatus shown in Fig. 45. In the 100–150 ml flask *K*, place 6–8 g of granulated zinc coated with copper* and about 20 ml of 4.5 *N* sulfuric acid free from arsenic. At the end of 10 minutes all the air should be expelled from the apparatus by the evolved hydrogen. Now cover the outlet *D*† with a piece of mercuric chloride paper and weight it down with a small piece of ground glass. According to the quantity of arsenic present, allow all or a part of the solution in *T* to flow into the flask *K*. After 20 minutes remove the test paper and compare the color of the spot produced with spots similarly obtained with known quantities of arsenic.

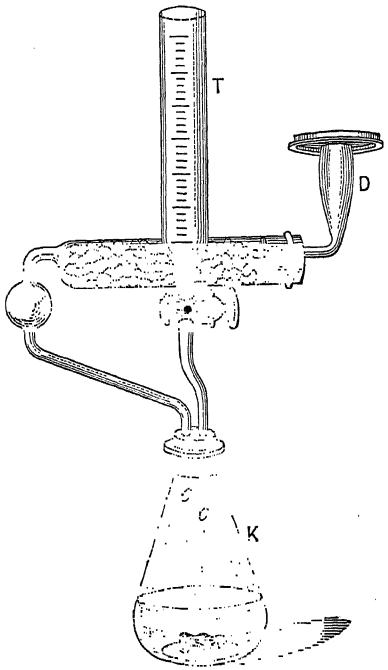

Fig. 45.

Prepare the disks of mercuric paper by dipping pieces of clean filter paper into a saturated solution of mercuric chloride and drying in an oven at 60°–70°.

Prepare the standards by a series of experiments with known quantities of arsenic. The spots thus obtained soon lose their color when exposed to moist air, but when dry can be kept in the dark for several days. An older standard is not reliable, but can be used to estimate the approximate quantity of arsenic and then, by making two or three standards with known quantities, the exact amount of arsenic can be determined. A con-

* Cf. Vol. I.

† For quantities of arsenic under 0.02 mg the upper diameter of the tube *D* should be 8 mm, and for larger quantities it should be 16 mm. The upper edge of the tube is ground perfectly flat.

venient standard solution of arsenious acid used in preparing the scale contains 20 mg of As_2O_3 in a liter. For less than 0.02 mg of As_2O_3 (= 1 ml of the standard solution) dilute the solution tenfold.

(*b*) Method of Sanger-Black

Place 10 g of chemically pure stick zinc, a few stannous chloride crystals, and a piece of platinum foil with several perforations in the 30-ml evolution bottle (Fig. 46). Add a measured volume of the arsenic solution, nearly fill the flask with 7 *N* sulfuric acid, and insert the stopper carrying the tubes *A*, *B*, and *C* as shown in the drawing. The tube *A* is 7 cm long and 1 cm wide and contains a few strips of filter paper that have been moistened with 5 per cent lead acetate solution, to remove traces of hydrogen sulfide that may be formed from sulfur in the zinc. The tube *B* is a little shorter than *A* and contains a wad of cotton moistened with 1 per cent lead acetate solution. The tube *C* contains a dry strip of mercuric chloride paper prepared by allowing strips of thick drawing paper to remain for an hour in 5 per cent alcoholic mercuric chloride solution, hanging the strips on glass rods and allowing them to dry in the air. After a few minutes the mercuric chloride paper begins to darken, and after 45 minutes a maximum depth of color is obtained. Compare the color with that produced similarly by known quantities of arsenic produced in the same way with the same apparatus.

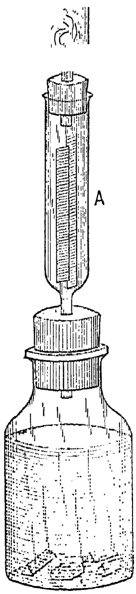

FIG. 46.

Figure 47 shows how the standard strips should look.

(*c*) Electrolytic Determination of Arsenic*

Instead of producing the arsine by the action of zinc and acid, it may be formed by cathodic reduction, $AsO_2^- + 6 \ominus + 7 H^+ \rightarrow AsH_3 \uparrow + 2 H_2O$. Thorpe passes the arsine through a heated tube and produces an arsenic mirror, but Hefti† allows the

* Cf. Bloxam, *Z. anal. Chem.*, **1**, 483 (1862); T. E. Thorpe, *Proc. Chem. Soc.*, **19**, 183 (1903); W. Thomson, *Manch. Memoirs*, **48**, No. 17 (1904); S. R. Tootmann, *Chem. Zentr.*, **1904**, I, 1295; H. J. S. Sand and E. Hackford, *Chem. Zentr.*, **1904**, II, 259.

† *Inaug. Dissert.*, Zürich, 1907.

gas to react with mercuric chloride paper. In both cases the apparatus devised by Thorpe (Fig. 48) can be used.

As cathode a perforated cone of thin lead foil, *K*, is recommended. Hang this upon the platinum wire that has been fused into the ground-glass stopper of the cathode compartment. As anode use platinum foil, 2 or 3 cm wide wrapped around the porous cell, *D*.

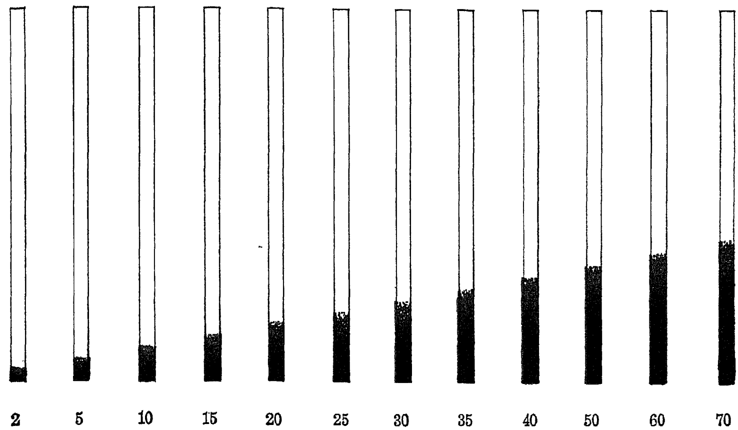

FIG. 47.

Procedure. — Pour pure, 4.5 N sulfuric acid into the porous cell *D*, and into the glass outer vessel, *E*. The level of the acid should be about 2 or 3 cm from the bottom in *D* and about 0.5 cm higher in *E*. For the colorimetric determination, pour the arsenic solution directly into the acid of the inner cell. It must be present as arsenious acid; cf. p. 211. For the production of mirrors, all the air must be expelled by hydrogen before the arsenic solution is added. The tube *C* should contain crystallized calcium chloride. Cover the outlet at *D* with a disk of mercuric chloride paper (see Method *a*) and electrolyze with a current of 2–3 amperes at about 7 volts. The analysis is finished at the end of 20

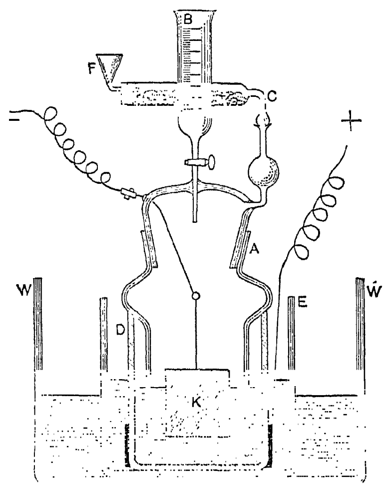

FIG. 48.

minutes. Estimate the quantity of arsenic by comparing the spot with a standard scale. (See Method *a*.) If the apparatus is connected with a horizontal delivery tube, Sanger's method can be used. (See Method *b*.)

Remark. — As cathode Thorpe recommends bright platinum foil and Hefti uses lead. Polished platinum does not hold arsenic back, but platinum with a rough surface does, and since bright platinum becomes dull with use, it is easily possible for low results to be obtained. Experiments performed by Hefti in the author's laboratory showed that zinc alloyed with a trace of copper or platinum, bright platinum foil, and lead did not hold back arsenic when used as the cathode; on the other hand, zinc in the presence of chloroplatinic acid and platinum foil with spongy platinum held back a considerable quantity of arsenic.

To determine arsenic in a mineral water, evaporate 100 ml to a small volume in a porcelain dish. Add a little sulfuric acid, reduce with sulfurous acid, expel the excess of the latter, and analyze by one of the above three methods.

Determination of Larger Quantities of Arsenic as Arsine

Method of F. Hefti

In the electrolysis of larger quantities of arsenic it was not possible, in the past, to recover all the arsenic as arsine; some arsenic was deposited upon the cathode in the form of the element arsenic and was not transformed into arsine by the further action of the electric current. The quantity of arsenic deposited as metal depends upon the potential of the electric current at the electrodes, the temperature, and the concentration of the arsenic solution. At high potentials, low temperature, and low concentration of the solution, the quantity of arsenic deposited becomes zero and the yield of arsine is then quantitative. The estimation of the latter is best accomplished iodometrically. If arsine is passed through a solution of iodine in potassium iodide, it is immediately oxidized to arsenic acid in the cold.

$$AsH_3 + 10\ NaHCO_3 + 4\ I_2 = Na_2HAsO_4 + 8\ NaI + 10\ CO_2 + 6\ H_2O$$

If the excess of iodine is titrated with sodium thiosulfate (see Iodometric Methods) it is possible to determine the quantity of iodine that has reacted with the arsine. If T milliliters of 0.1 N iodine were used at the start, and t milliliters of 0.1 N thiosulfate solution were used for the titration, then the quantity of arsenic or arsenic trioxide present is

$$(T - t) \times 0.000937 \text{ g arsenic}$$
$$(T - t) \times 0.001237 \text{ g } As_2O_3$$

The apparatus necessary is shown in Fig. 49. The decomposition cell is also shown in Fig. 50 and consists of a wide U-tube capable of holding 120 ml of solution. The tube is made in two halves, the edges of the bottom being ground so that they fit tightly together. Between these edges place a piece of thin parchment paper and fold the extending edges over one side of the tube. Bind the two halves of the U-tube together by a piece of rubber tubing which also holds the parchment paper in place. Wire this tubing tightly in place, taking care that the edges of the parchment paper are also covered by the wire. In one arm of the tube (the anode compartment) which remains open during the whole experiment, suspend a platinum plate electrode as anode, and tightly stopper the other arm (the cathode compartment) with a three-holed rubber stopper. Through one hole insert a glass tube

containing mercury, and with a platinum wire sealed into the bottom; from this suspend a plate electrode of lead foil to serve as cathode. Make the wire from the negative pole of the battery dip into the mercury. Through the second hole in the stopper insert a gas delivery tube leading to the absorption vessel *A*. The third hole in the stopper carries a tube that leads to the Erlenmeyer flask *E* containing a little water, which, in turn, is connected with the empty flask *F*, and the latter with the rubber tubing shown in Fig. 49. This tubing leads to the hood. Such an

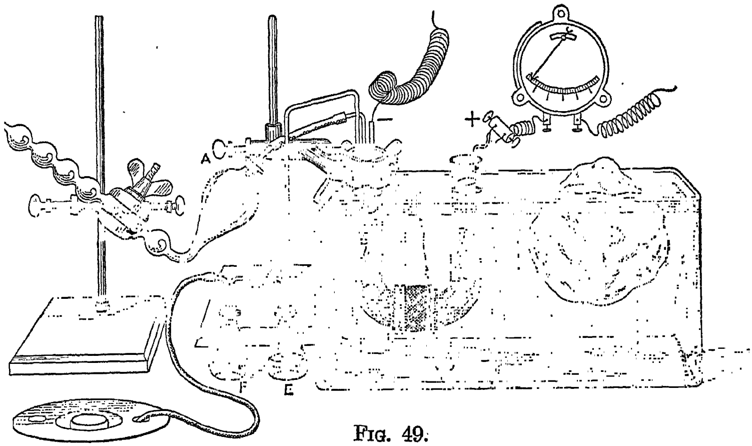

FIG. 49.

arrangement provides for the regulation of the pressure in the cathode space. If the pressure there exceeds that of the anode space, a part of the arsenic solution will pass into the anode compartment and be lost in the analysis. By applying suction at the extreme end of the absorption apparatus so that bubble after bubble of air passes through the Erlenmeyer, it is easy to overcome the pressure in the absorption vessel without having diminished the pressure in the cathode compartment enough to tear the parchment membrane.

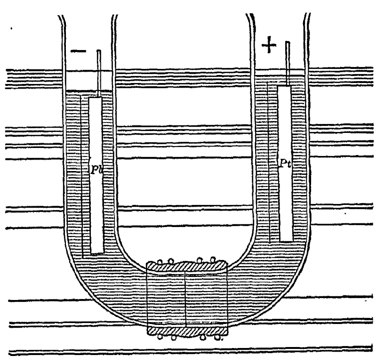

FIG. 50.

Procedure. — The arsenic solution to be tested must contain all the arsenic in the trivalent condition. First of all, fill the anode compartment within 3 cm of the top with 2 *N* sulfuric acid, pour the arsenite solution into the cathode compartment and fill this within 3.5 cm of the top, leaving the level of the liquid about 0.5 cm lower than on the other side of the U-tube; the concentration of the arsenic solution in the U-tube, after this dilution with acid, should not exceed 80 mg As_2O_3 in

50 ml of solution. Place the U-tube in ice-water and connect the gas delivery tube with two ten-bulb absorption tubes, of which only one is shown in the drawing. Into the first absorption tube place an accurately measured volume of 0.1 *N* iodine solution, and into the second tube, which is not shown in the drawing, 10 ml of standard 0.1 *N* sodium thiosulfate solution diluted with 40 ml of water. The purpose of the sodium thiosulfate solution is to catch any iodine that may escape from the first absorption tube. While the absorption vessels are being filled, the arsenic solution should be in the ice-water, and its temperature should be about 0° when the analysis is ready to begin. Apply gentle suction at the end of the second absorption tube, close the electric circuit, using 2–3 amperes as in the preceding method of analysis, and regulate the suction so that bubble after bubble of air slowly streams through the pressure regulator and into the cathode compartment throughout the duration of the electrolysis. Moreover, take care that sufficient ice remains in the cooling bath. When all the conditions are maintained satisfactorily, the liquid in the cell should remain perfectly clear, or at the worst be colored only by a slight brownish turbidity which eventually disappears. If a black turbidity is formed that settles to the bottom of the U-tube, something has gone wrong and it is useless to continue the experiment. In a normal experiment, the evolution of the arsine is finished in an hour, if not more than 50 mg of As_2O_3 is present. Then turn off the current and pour the contents of the two absorption tubes (first the iodine and then the thiosulfate solution) into a beaker containing 5 ml of a saturated solution of pure $NaHCO_3$. Titrate the excess of iodine with 0.1 *N* sodium thiosulfate solution using starch solution as indicator. If on mixing the contents of the two absorption bulbs the solution is decolorized, finish the titration with 0.1 *N* iodine.

This method can be carried out very easily and gives accurate results in the presence of iron, so that it is suitable for a rapid determination of the arsenic present in iron minerals.

W. D. Treadwell* recommends a simpler apparatus, shown in Fig. 51. The glass beaker is about 14 cm tall. The cathode compartment, from which the arsine is evolved, consists of a glass tube about 12 cm tall and 2.5 cm wide, fastened at the bottom, by means of the short piece of rubber tubing, *G*, to the porous diaphragm *T* of the same outside diameter. This bottom part is made by sawing off the bottom of an ordinary porous cell, leaving an edge of only about 1 cm. The glass tubing is shown separated from the diaphragm in the drawing merely

* *Elektroanalytische Methoden* (1915).

to indicate that the two tubes are joined at this place. As cathode, use a piece of lead wire wound into a spiral as shown by K in the drawing. Thicken the lead wire at the top so that it fits tightly into the glass tubing of H, thus preventing loss of arsine through this tubing. Outside of this cathode compartment place an ordinary platinum gauze electrode to serve as anode. Pour $4\,N$ sulfuric acid into the beaker and cover the anode with this electrolyte. Pour the solution to be tested for arsenic into the cathode compartment and have the level of the sulfuric acid in the beaker about 2 cm higher than that of the solution around the cathode. Close the cathode compartment with a stopper carrying the cathode and the gas delivery tubing. Place the beaker in ice-water to keep the temperature below 10°, and electrolyze as described above. The absorption flask J should contain 25 ml of $0.1\,N$ iodine solution, and it should be connected with a similar absorption flask containing 25 ml of $0.1\,N$ thiosulfate. Both solutions must be measured carefully from a pipet or buret.

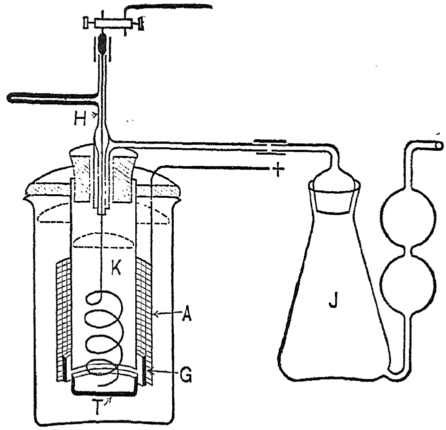

FIG. 51.

Determination of Arsenic in Mispickel

Fuse 1 g of the finely powdered mineral in a nickel crucible with 6 g of sodium carbonate and 1 g of potassium nitrate. Extract the resulting melt with hot water and wash the residue (Fe_2O_3, NiO) with hot sodium carbonate solution. To the filtered solution add 200 ml of water saturated with SO_2 to reduce the arsenic, boil to expel the excess of SO_2, allow to cool, dilute to 500 ml with water and sulfuric acid so that the entire solution is about $2\,N$ in H_2SO_4, and determine the arsenic as outlined above, using one-tenth of the solution.

Instead of extracting the melt with water, it may be treated with dilute sulfuric acid, whereby all the iron goes into solution. After this solution has been reduced with sulfurous acid, the analysis of an aliquot part gives the same result as when the first procedure is followed.

ANTIMONY, Sb. At. Wt. 121.76

Forms: Sb_2S_3, Sb_2O_4, and Sb

1. Determination as Trisulfide, Sb_2S_3

(*a*) Method of F. Henz*

The best method for the determination of antimony is unquestionably the following:

Conduct hydrogen sulfide for 20 minutes into the cold solution, which should be about *N* in HCl, then, without stopping the current of hydrogen sulfide, slowly heat the solution to boiling and continue the stream of hydrogen sulfide for 15 minutes more. Remove the flame, allow the precipitate to settle, and decant through a Gooch crucible which has been heated at 280–300° and weighed. Wash the precipitate four or five times by decantation with 50–75 ml of hot, very dilute acetic acid into which hydrogen sulfide has been passed. Wash on the filter with the same liquid until all chloride is removed. At first the filtrate runs through perfectly clear, but after all the mineral acid has been removed, the filtrate shows a slightly orange tint, owing to an unweighable amount of the antimony sulfide passing through in colloidal solution. As soon as this point is reached, stop the washing.

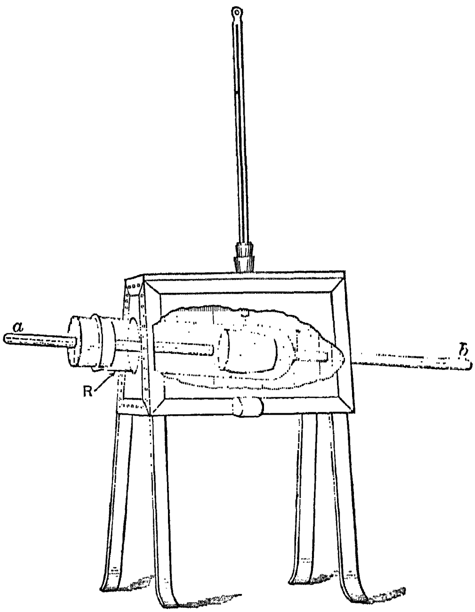

FIG. 52.

Place the crucible, after the precipitate has been dried as much as possible by suction, in the tube *R*, Fig. 52, which is fitted to a drying oven (about 18 cm long and 10 cm high and covered with asbestos paper). Close the tube *R* with a rubber stopper that holds a glass delivery tube, and push *R* into the drying closet until the end of the stopper is reached. To protect the rubber stopper during the sub-

* F. Henz, *Z. anorg. Chem.*, **37**, 18 (1903).

sequent heating, fit a Rose crucible cover against it, holding it in place by wrapping the tube *a* with a strip of asbestos paper.

Expel all air from the tube by a stream of dry, air-free carbon dioxide* and heat for 2 hours at 100° to 130°. Inasmuch as the tube *R* extends so far into the drying oven, there is no danger of water condensing in the tube; it is all expelled as vapor at *b*. The precipitate is now dry and the air completely expelled from the heating tube.

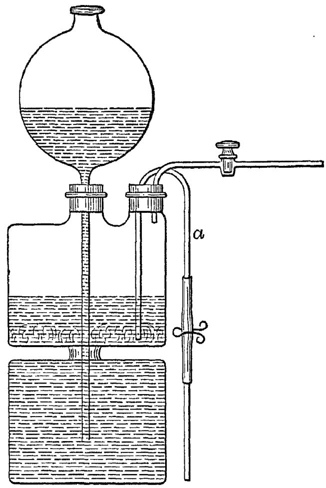

FIG. 53.

Now withdraw the tube *R* a little ways out of the oven, about 5 cm, as shown in the drawing, raise the temperature to 280–300°, and keep it there for 2 hours.

Hereby some sulfur is volatilized and collects in the tube *R* outside the oven. The orange pentasulfide is also completely changed into the black antimony trisulfide by this heating.† Allow the crucible to cool in the stream of carbon dioxide, transfer to the balance case,‡ let stand half an hour and weigh.

* In order to obtain accurate results it is necessary to have the carbon dioxide perfectly free from air. This may be prepared by the use of the Kipp generator as modified by Henz (*Chem. Ztg.*, **1902**, 386); see Fig. 53.

This differs from the ordinary form of the Kipp apparatus only as regards the siphon tube *a*; but herein lies a distinct advantage. The apparatus is charged as follows: First of all, place pieces of pure marble in the middle compartment, open the stopcock, and pour water through the upper compartment until it begins to run out through the stopcock, which is then closed. By this means all the air has been expelled from the lower parts of the apparatus and it remains only to introduce the hydrochloric acid. To accomplish this, allow the water to run out through the siphon while pouring 2.5 *N* hydrochloric acid in at the top of the generator. As soon as carbon dioxide begins to be evolved close the tube *a*, and the apparatus is ready for use. When the acid has become too weak, remove it through the siphon, pouring in a fresh supply at the top; there is no need of taking the apparatus apart during this operation. It is obvious that the same apparatus can be employed to advantage for generating hydrogen or hydrogen sulfide.

† According to Paul (*Z. anal. Chem.*, **31**, 540 (1892)), the transformation of antimony pentasulfide can be accomplished at 230° but it is much more rapid at 280–300°. It is more difficult to replace the air completely with carbon dioxide in Paul's drying oven.

‡ Roll up a piece of writing-paper and place it in the tube *R*, so that the crucible does not come in contact with any of the sulfur sublimate, on withdrawing it. Remove the crucible with the paper.

The black antimony trisulfide is not at all hygroscopic. A further heating in the current of carbon dioxide will rarely show any change in weight.

(*b*) Method of Vortmann and Metzl*

When antimony is precipitated by hydrogen sulfide from a hot solution which is strongly acid with hydrochloric acid, the sulfide eventually becomes grayish black in color, is crystalline, and can be filtered easily and washed with water without the slightest tendency to pass into the hydrosol condition.

To each 100 ml of neutral solution in an Erlenmeyer flask, add 24 ml of 12 N hydrochloric acid. Heat to boiling, and subject the hot solution to the action of hydrogen sulfide gas. Place the Erlenmeyer flask containing the solution in a dish of boiling water and keep the water boiling during the precipitation. It is advisable to introduce the hydrogen sulfide gas quite rapidly at first, but towards the end a slow stream is sufficient. The antimony sulfide as it comes down is yellow at first, but as the precipitation proceeds, it becomes redder; gradually it becomes heavier and denser, assumes a crystalline form and becomes darker and finally black in color. The transformation into the crystalline form is hastened by shaking the flask. At first, while the precipitate is of a yellowish color, there is no need of shaking the flask, but later on it is very desirable to do so. The shaking, however, should not be too violent, as otherwise some of the precipitate is likely to adhere to the upper portions of the flask and escape the transformation. The reaction requires 30–35 minutes. Finally a heavy, dense, crystalline precipitate of antimony trisulfide is obtained which settles well and permits a rapid filtration. Dilute the solution with an equal volume of water, allowing it to flow around the walls of the flask in order to wash down any adhering sulfide. The dilution almost always causes the formation of a slight yellow turbidity. The reason for this is that a little of the antimony is held in solution by the strong acid and as the solution is diluted this is caused to precipitate by the dissolved hydrogen sulfide. Once more shake the flask, replace it in the vessel of boiling water, and introduce more hydrogen sulfide. In 2 or 3 minutes the solution above the precipitate will become clear. Filter through a Gooch crucible, wash with water to remove the acid, then with alcohol, place in the drying-oven, and heat as described under (*a*).

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* *Z. anal. Chem.*, **44**, 526 (1905).

2. Determination as Tetroxide, Sb_2O_4 (Bunsen)

This method is based upon the fact that antimony pentoxide, when ignited at a definite temperature, changes into Sb_2O_4. Bunsen,* who first proposed the method, later abandoned it because his assistant succeeded in volatilizing more than 0.1 g of the precipitate by heating it over the blast lamp.† Brunck,‡ Rössing,§ and Henz‖ have shown, however, that accurate results can be obtained. In 1897, Baubigny¶ discovered that antimony pentoxide is converted quantitatively into the tetroxide at a temperature of 750°–800°. The literature is conflicting with regard to the volatility of Sb_2O_4. This oxide is often regarded as antimonous antimonate with one atom of antimony in the trivalent condition and the other atom in the quinquevalent state. The oxide Sb_2O_4 is very easily reduced and Sb_2O_3 volatilizes quite rapidly at 1000° (0.35 g in 30 minutes).

Procedure. — In most cases it is desired to determine the amount of antimony present in a mixture of its tri- and pentasulfides, or in a mixture of one or the other of the two compounds with sulfur. It is best to proceed as follows: Precipitate the sulfide of antimony from a hot solution, wash the precipitate first with hot water, then with alcohol, afterwards with a mixture of alcohol and carbon disulfide (in order to remove the sulfur),** again with alcohol, and finally with ether. Then dry the precipitate, separate the bulk of the precipitate from the filter and place it upon a watch glass. Put the filter in a small porcelain dish and boil it with a little freshly prepared ammonium sulfide solution stirring constantly with a glass rod. Pour the resulting solution through a small filter into a 30-ml porcelain crucible, and treat the filter repeatedly with ammonium sulfide until it is no longer colored brownish red at the edge of the paper, where it begins to dry; the extraction of the antimony sulfide is then complete. Evaporate the solution in the crucible to dryness and add the main part of the precipitate. To oxidize the antimony sulfide, Beckett places the crucible, with a dish of fuming nitric acid beside it, under a bell-jar and allows it to stand over night. The vapors of fuming acid slowly oxidize the precipitate in the crucible and in the morning it is possible to complete the oxidation by means of nitric acid (*d.* 1.4) without the reaction being too violent. Heat the crucible on the water-bath until the precipitate becomes white and the greater part of the acid is expelled. Add a little water and, with stirring, enough concentrated ammonia to give an

* *Ann. Chem. u. Pharm.*, **106**, 3 (1858).

† *Ibid.*, **192**, 316 (1878).

‡ *Z. anal. Chem.*, **34**, 171 (1895).

§ *Ibid.*, **41**, 9 (1902).

‖ *Loc. cit.*

¶ Compt. rend., **124**, 499 (1897).

** Thiele, *Ann. d. Chem. und Pharm.*, **263**, 372.

alkaline reaction. Evaporate the contents of the crucible to dryness on the water-bath, carefully heat in an air-bath (Fig. 14, p. 37) until no more fumes of sulfuric acid are evolved, and then for half an hour at 800° in an electric oven. Cool in a desiccator, transfer the crucible quickly to a glass-stoppered weighing beaker, allow to stand 20 minutes in the balance case, and then weigh. Repeat the ignition and weighing until a constant weight is obtained.

3. Determination of Antimony as Metal

Antimony may be deposited from acid solutions by means of the electric current; the metal, however, does not adhere well to the electrode, so that this method cannot be used for its quantitative determination. On the other hand, the following method is suitable; it was first proposed by Parrodi and Mascazzini,* then modified by Luckow,† and afterwards improved by Classen and Reiss.‡ According to the experience in the author's laboratory, it is not so accurate as the trisulfide method.

If a solution of sodium or ammonium thioantimonite, or antimonate, containing not more than 0.2 g Sb in a volume of about 140 ml is subjected to electrolysis with a current of 1–1.5 amperes at 65° for 90 minutes, the antimony will be deposited upon a platinum dish, which has been etched by treatment with dilute aqua regia, as steel-gray, metallic antimony, and the deposit adheres so firmly that it can be dried and weighed without loss. The chief condition for the success of this operation is the absence of polysulfides. If these substances are present the antimony is incompletely deposited and in some cases not at all, or the deposited antimony may pass into solution, on account of being oxidized to sodium thioantimonite by means of the sodium polysulfide which is formed at the anode during the electrolysis: $2\ Sb + 3\ Na_2S_2 = 2\ Na_3SbS_3$.

It is necessary, therefore, to prevent the formation of polysulfides during the electrolysis. For this reason Lecrenier§ added sodium sulfite to the bath, whereby the polysulfide is transformed into thiosulfate: $Na_2S_2 + Na_2SO_3 = Na_2S_2O_3 + Na_2S$.

Ost and Klapproth|| carry out the electrolysis with the aid of a diaphragm to keep the polysulfide away from the cathode.

It is better, however, to make use of potassium cyanide for this purpose.¶ $Na_2S_2 + KCN = Na_2S + KCNS$.

Procedure. — Usually the antimony is first isolated as the sulfide, which is either precipitated by hydrogen sulfide from acid solution or obtained by acidifying an alkaline solution of the sulfo-salt. Dissolve the filtered and washed precipitate, corresponding to not over 0.2 g Sb, on the filter by pouring pure sodium sulfide solution (*d.* 1.14) over

* *Z. anal. Chem.*, **18**, 587 (1879).

† *Ibid.*, **19**, 13 (1880).

‡ *Ber.*, **14**, 1629 (1881); **17**, 2474 (1884); **18**, 408 (1885); **27**, 2074 (1894).

§ A. Lecrenier, *Chem. Ztg.*, **13**, 1219 (1889).

|| *Z. angew. Chem.*, **1900**, 828.

¶ Cf. A. Fischer, *Ber.*, **36**, 2048 (1903); *Z. anorg. Chem.*, **42**, 363 (1904); Hollard, *Bull. soc. chem.*, **23** [3] 292 (1900); F. Henz, *Z. anorg. Chem.*, **37**, 31 (1903).

it. Catch the solution as it runs through the filter in a weighed platinum dish with etched inner surface. After washing the filter with the sodium sulfide solution, the total volume of the liquid in the platinum dish should not be above 80 ml; if less than this, add more sodium sulfide solution. Dilute the solution with 30 ml of 10 per cent, freshly prepared pure potassium cyanide solution and dilute to 125 ml. Heat to 65° (not over 70°) and electrolyze with a current of 1.2–1.3 amperes and electrode potential of 2–3 volts. After 1.5–2 hours all the antimony will be upon the cathode in the form of a firmly adhering, light gray deposit.* Now, without breaking the circuit, siphon off the electrolyte, while adding water until the current ceases to pass through the liquid (the voltmeter connected as ammeter points to the zero reading). Remove the cathode, wash thoroughly with water, then with 95 per cent alcohol, dry at about 80°, cool in a desiccator, and weigh. The results by this method are usually a little high.

Cleaning the Electrodes. — Ost † recommends heating with a mixture of equal parts concentrated nitric acid and a saturated solution of tartaric acid. The antimony will also dissolve readily by heating with a solution of alkali polysulfide.

TIN, Sn. At. Wt. 118.7

Forms: SnO_2, Sn

1. Determination as Tin Dioxide, SnO_2

Two cases are to be distinguished:

(*a*) *The Tin is Present as Metal (in an Alloy).*
(*b*) *The Tin is Present in Solution.*

(*a*) The Tin is Present in an Alloy

Procedure. — Dissolve 0.5 g of borings in a small beaker with 15 ml of 6 *N* nitric acid, *d.* 1.2. Evaporate the solution just to dryness on the water-bath, and remove the beaker as soon as this stage is reached. Treat the residue with 20 ml of 2 *N* nitric acid, heat to boiling, and decant off the solution through a hardened filter paper. Repeat this treatment. Complete the washing by boiling and decanting with 1 per cent ammonium nitrate solution. Keep as much of the precipitate

* To make sure that the deposition is complete, the liquid may be transferred quickly to a second dish and electrolyzed for half an hour longer. It is seldom that any gain in weight will be shown by this dish.

† *Z. angew. Chem.*, **1901**, 827.

as possible in the original beaker, and the total volume of the filtrate under 150 ml. Examine the first portions of the filtrate for metastannic acid, refilter if necessary, and remove each successive portion from below the funnel before adding more wash water. Wash the precipitate with 1 per cent NH_4NO_3 solution until a portion of the filtrate will give no test for copper or lead on adding a little ammonium sulfide solution (or for copper with $K_4Fe(CN)_6$ solution). Save the precipitate for the tin determination.

To determine the copper and lead electrolyze this solution, and the nitric acid solution obtained below, with platinum gauze electrodes with a current of 0.25 ampere for 4 to 6 hours and then one of 0.1 ampere for 18 to 20 hours. The copper will be deposited on the cathode as metallic copper and the lead upon the anode as PbO_2. (See p. 201.)

Ignite the precipitate at first gently and finally strongly, over a Méker burner or a blast lamp, in an open porcelain crucible, and weigh as SnO_2.

The tin dioxide thus obtained is never pure; it always contains small amounts of other oxides and should be purified by one of the following methods:

(*a*) After weighing, add to the precipitate six times as much of a mixture consisting of equal parts sodium carbonate and pure sulfur. Heat in a covered porcelain crucible over a small flame until the excess of sulfur is almost entirely removed. This point is easily recognized by there being no longer any odor of SO_2 and no blue flame of burning sulfur evident between the cover and the crucible. Cool and dissolve the melt in a little hot water; the tin goes into solution* as sodium thiostannate (cf. Vol. I), together with some copper and iron. Treat the deep brown liquid, therefore, with sodium sulfite† solution until it becomes only slightly yellow in color; any iron or copper, etc., will now be precipitated quantitatively as sulfides. Filter off the latter and wash first with water to which a little sodium sulfide has been added and finally with hydrogen sulfide water. As a rule the amount of insoluble sulfide formed by this treatment is so small that after drying it can be ignited in an open porcelain crucible and changed to oxide without introducing any appreciable error. If this weight is subtracted from the original amount of impure stannic oxide, the weight of pure stannic oxide will be obtained. If, however, the amount of impurity present with the residue of metastannic acid is large, the different metals must be sepa-

* Frequently a single fusion with sodium carbonate and sulfur is insufficient; this is recognized by obtaining a sandy residue insoluble in water. In this case filter off the residue, wash, dry, and repeat the fusion.

† The sodium sulfite changes the sodium polysulfide to monosulfide, in which copper and iron sulfides are insoluble.

rated, according to one of the methods for the separation of the sulfobases, the weight of each oxide determined separately, and the sum of their weights subtracted from the original weight of the tin dioxide. Instead of determining the amount of impurity present with the tin dioxide, the filtrate from the insoluble sulfides can be acidified with acetic acid and the tin precipitated as yellow stannic sulfide, which, after it has completely settled, can be filtered off and changed by careful ignition in an open porcelain crucible to tin dioxide, as described on p. 226, and weighed as such.

(*b*) Instead of igniting the precipitate, wash it into a porcelain evaporating dish, evaporate on the water-bath almost to dryness, and then treat with 1 ml of pure sodium hydroxide solution and 10–15 ml of saturated sodium sulfide solution. Cover the evaporating dish with a watch glass, and heat for about 45 minutes on the water-bath, whereby all the tin should pass into solution, and the other metals remain undissolved as sulfides. Filter and wash with very dilute sodium sulfide solution.

The filter upon which the metastannic acid was filtered still retains some of the precipitate. Spread it out, therefore, in a second small evaporating dish, cover with about 1 ml of sodium sulfide solution, and heat on the water-bath. After half an hour, all the tin should be dissolved. Pour the solution through a small filter and wash the latter with a little hot water.

Dry the two filters, ignite in a porcelain crucible, treat the ash with a small quantity of strong nitric acid, and add the resulting solution to that obtained by dissolving the alloy in nitric acid.

For the determination of the tin, combine the two solutions containing sodium thiostannate, make acid with acetic acid, and boil to expel the hydrogen sulfide. Filter off the precipitated stannic sulfide, wash once with water to remove the most of the alkali salts, then transfer back to the original beaker and dissolve in 10 ml of 50 per cent potassium hydroxide solution and 1 g tartaric acid; these quantities suffice for 0.1–0.2 g of tin. To the solution, add pure 30 per cent hydrogen peroxide (Perhydrol, Merck) until the yellow liquid becomes perfectly colorless, then add 1 ml in excess. Boil the solution for 10 minutes to make sure that the oxidation is complete and that the excess of peroxide is decomposed. As soon as no more bubbles of oxygen are evolved, allow the solution to cool somewhat and add cautiously 15 g of oxalic acid dissolved in a little hot water. Electrolyze the hot solution as described on p. 227.

The precipitated stannic sulfide, as obtained above by acidifying the sodium thiostannate solution, may be ignited in a porcelain crucible and

weighed as SnO_2. The results are usually a little high and the method is not as accurate as the electrolytic determination. See below; β.

(b) The Tin is Present in Solution

(α) *The Solution Contains Tin Only*

If the solution contains only tin in the form of stannic salt (chloride or bromide), add a few drops of methyl orange indicator solution and then ammonia until the pink color of the indicator is changed to yellow. Add 24 g of ammonium nitrate and dilute the solution to a volume of 300 ml. Heat to boiling, filter after the precipitate has settled, wash with hot 2 per cent ammonium nitrate solution, ignite in an open porcelain crucible, and weigh as SnO_2.

Remark. — If the solution contains non-volatile organic acids, this method cannot be used for the determination of tin. In this case the tin must be first precipitated as sulfide by means of hydrogen sulfide (see below). If the tin is not in solution as stannic salt but as stannous salt, the solution must be first oxidized by the addition of bromine water until a permanent yellow color is obtained, after which the solution can be neutralized with ammonia and treated as above described.

According to J. Löwenthal,* tin can be precipitated from slightly *acid* stannic chloride or bromide solutions by boiling with ammonium nitrate. Add methyl orange to the solution and then ammonia until a yellow solution is obtained;† now add dilute nitric acid, drop by drop, until the solution just becomes pink again, and continue as described above.

(β) *The Solution Contains, besides Tin, Metals of the Ammonium Sulfide Group or Organic Substances*

In this case, independent of whether the tin is present in the form of stannic or stannous salts, conduct hydrogen sulfide into the dilute solution until it is saturated with the gas; allow the solution to stand until the odor of hydrogen sulfide has almost disappeared and then filter. Wash the precipitate with a 2 per cent ammonium nitrate solution, dry, transfer as completely as possible to a porcelain crucible, and add the ash of the filter. Heat the tin sulfide at first gently with the flame well in front of the inclined open crucible to avoid loss by decrepitation, and afterwards with the flame at the base of the crucible until the odor of sulfur dioxide is no longer perceptible. Now raise the temperature gradually until finally the full heat of a good Teclu or Méker burner is obtained. As tin dioxide holds fast to some sulfuric acid with great tenacity, after cooling the crucible somewhat add a piece of ammonium

* *J. prakt. Chem.*, **56**, 366 (1852).

† The excess of acid cannot be removed by evaporation on account of the volatility of stannic chloride.

carbonate the size of a pea. Again heat and weigh as SnO_2. Repeat the heating with ammonium carbonate until a constant weight is obtained.

Remark. — F. Henz* in testing this method always obtained results which were a little too high. This is due to the fact that it is difficult to wash the stannic sulfide precipitate free from sodium salts. It is best, therefore, to dissolve the well-washed stannic sulfide precipitate in a little sodium sulfide, transform the thiostannate into stannioxalate, and determine the tin by electrolysis (see below), or as oxide by the method of Löwenthal (see above directions).

2. Determination of Tin as Metal

The electrolytic deposition of tin from a solution of the ammonium stannioxalate gives excellent results. It is necessary, however, to have free oxalic acid always present while the solution is undergoing electrolysis. During the process, ammonium oxalate is changed by anodic oxidation into ammonium bicarbonate and carbon dioxide:

$$C_2O_4^{--} + 2\,H_2O + 2\,\oplus = 2\,HCO_3^{-} + 2\,H^{+}$$
$$HCO_3^{-} + H^{+} \rightleftarrows H_2O + CO_2\uparrow$$

and the solution will smell of ammonia as a result of the hydrolysis of ammonium carbonate. When this point is reached no more tin is deposited. The ammonia often precipitates some stannic acid, which escapes the electrolysis. It is necessary, therefore, to avoid letting the bath become ammoniacal, and this is best accomplished by adding a little solid oxalic acid from time to time.

In the following method the electrolysis is accomplished in a potassium oxalate solution. Not more than 0.3 g of tin should be present in the solution analyzed.

Procedure. — In the course of an analysis it is usually necessary to precipitate the tin from a solution of alkali thiostannate. This is best accomplished as follows: Decompose the thio-salt by acidifying with acetic acid, boil to expel hydrogen sulfide, and dissolve the sulfide by adding 15 g of solid potassium hydroxide. Oxidize by adding perhydrol (concentrated H_2O_2) drop by drop. At first the color of the solution deepens but eventually it becomes colorless. Finally boil 10 minutes, add 15 g of oxalic acid, and boil 10 minutes more. Then dilute to about 150 ml, heat to 65°, and electrolyze with a current of 1 ampere and 3–4 volts potential at the electrodes; at the end of about 6 hours all the tin will have been deposited upon a gauze electrode. Wash the deposit with water, exactly as prescribed for nickel on p. 143, then with alcohol, dry by holding above a flame, cool in a desiccator, and weigh. The results are excellent.

Remark. — If ammonium oxalate is used in place of the potassium oxalate, the electrolysis requires more time (8 to 10 hours). By the addition of hydroxylamine the duration of the electrolysis is shortened (Engel).

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* *Z. anorg. Chem.*, **37**, 39 (1903).

If the solution becomes turbid during the electrolysis, insufficient caustic potash solution was used. Add 2–3 g of potassium hydroxide to dissolve the turbidity.

Separation of Arsenic, Antimony, and Tin from the Members of the Ammonium Sulfide Group

The separation is effected by passing hydrogen sulfide into the acid solution of the above metals whereby arsenic, antimony, and tin are precipitated as sulfides while the remaining metals remain in solution.

From an alloy, or the solid thio-salts of the above metals, arsenic, antimony, and tin may be readily volatilized by heating in a stream of chlorine; the chlorides of these three metals are readily volatile, whereas those of the remaining metals are only difficultly so.

Separation of Arsenic, Antimony, and Tin from Mercury, Lead, Copper, Cadmium, and Bismuth

The qualitative analysis of a mixed sulfide precipitate containing the above metals has been given in Vol. I (pp. 289, 294): in Method A, the precipitate is treated with sodium polysulfide; in Method B, ammonium polysulfide is used. As a result of the treatment, the sulfides of As, Sb, and Sn pass into solution, together with Hg if Na_2S_2 is used, Cu, Pb, Bi, and Cd remaining insoluble. If $(NH_4)_2S_2$ is used, Hg is included in the Cu group.

These procedures, though satisfactory from a qualitative point of view, do not effect a complete separation of the eight elements, and the quantitative analysis of a sulfide precipitate containing them all is a very complex problem. No simple process of general applicability can be given. The chief difficulties are:

1. Generally speaking, slightly incomplete extraction of tin and antimony from the mixed precipitate, necessitating a repetition of the procedure.
2. Partial solubility of copper and bismuth sulfides in alkaline polysulfides.
3. Insolubility of stannous sulfide in alkaline monosulfide, and incomplete extraction of antimony bisulfide by that reagent.
4. In presence of mercury, formation of mixed or complex sulfides of mercury with cadmium, tin, or copper, which modifies the reactions of these metals.

However, the simultaneous presence of all the above metals in one and the same substance is so rare an occurrence that it may be ruled out for practical purposes. In particular, mercury is not abundant in nature, and seldom used in alloys; its principal ore, cinnabar, may be found associated with sulfides of Fe, Cu, As, Sb, and Pb. The mercury determination in such ores is conducted by a volatilization process (cf. p. 183). In Eschka's method, the powdered ore is mixed with pure iron filings in a tall porcelain crucible supported by a well-fitting perforated asbestos plate so that only the lower one-third of the crucible projects below the plate. The crucible is closed with a tight-fitting concave gold lid filled with water. The bottom of the crucible is heated by a small flame. After cooling, the lid is removed, washed with alcohol, dried for a very short time, and weighed. The lid is then gently ignited and again weighed, the difference giving the mercury.

Cadmium is another element which is rarely met with in minerals other than zinc ores, in which it occurs in small quantities. It is an important constituent of certain fusible alloys: thus, Wood's metal consists of Bi, Cd, Sn, and Pb. Its analysis is

conducted like that of tin alloys (p. 223), the tin being separated as insoluble metastannic acid by treatment of the alloy with nitric acid. The nitrates of the other metals are converted into chlorides, and the lead chloride is collected as a residue insoluble in alcohol (p. 189). Bismuth is then precipitated as oxychloride; the cadmium is left in solution, from which it is recovered as sulfide, and this is converted into and weighed as sulfate (p. 198).

The metals other than mercury and cadmium are more frequently found together, and their separation will now be considered.

Separation of Arsenic, Antimony, and Tin from Lead, Bismuth, and Copper

The separation is carried out, as in qualitative analysis, by treatment with alkaline sulfide, forming soluble thio-salts of As, Sb, and Sn and insoluble sulfides of Pb, Cu, and Bi. It is generally preferable to use sodium sulfide; if Sb preponderates, potassium sulfide should be used, as the sodium salt of complex Sb salts are sparingly soluble; ammonium sulfide is used in separations affecting mercury.

The best separation is obtained if all the metals are in solution (case *a*); if they are in the form of a sulfide precipitate, the separation to be quantitative may have to be repeated (case *b*). If the metals are present as an alloy, low-temperature fusion with sodium sulfide is very convenient and effective (case *c*). Lastly, if insoluble or complex compounds have to be treated, fusion with sodium carbonate and sulfur is recommended (case *d*).

(*a*) *The Metals are in Solution.* — The metals should be in their higher state of oxidation (solution in *aqua regia*, or chloride solution treated with potassium chlorate or nitric acid). Add at least six times as much tartaric acid as there are metals present, and a slight excess of sodium hydroxide. Dilute to about 100 ml, pour the hot solution drop by drop, while stirring, into a hot solution of 5 to 10 g of sodium sulfide in 100 ml of water. Digest on the water-bath for half an hour, pass hydrogen sulfide through the liquid, allow the precipitate to settle, filter, and wash the precipitate thoroughly with dilute sodium sulfide solution.

(*b*) *The Metals are Contained in a Sulfide Precipitate.* — Heat the precipitate with a solution of 5 to 10 g of sodium sulfide in less than 50 ml of water. After boiling for a minute, allow the precipitate to settle on the water-bath, and if it shows a yellow color, treat with sodium sulfite solution (p. 224), stir, dilute with 100 ml of hot water, and set aside on the water-bath for half an hour. Filter off the precipitate and wash it with dilute sodium sulfide solution. Unless it is quite small, it is advisable always to retreat the precipitate, by dissolving it in aqua regia and applying procedure (*a*). Combine the filtrates (containing As, Sb, Sn).

(*c*) *The Metals Occur as an Alloy.* — White alloys (lead or tin base bearing metals) and copper alloys are most commonly met. In the case of white alloys, oxidize 1 g of sawings with nitric acid in a

porcelain dish, and evaporate to dryness. Triturate the residue with a flattened glass rod, mix with 10 g of sodium sulfide crystals and 0.2 g of powdered sulfur, and gently heat the covered dish so that the salt melts in its water of crystallization. Continue the digestion for half an hour; dissolve the product in 100 ml of hot ammonium nitrate solution. After another hour's digestion, collect the precipitate and wash it with dilute sodium sulfide solution. The filtrate contains all the tin and antimony (arsenic); the residual lead sulfide is free from these metals.*

In the case of copper alloys, separate the tin and antimony from the remaining metals by treating the alloy with nitric acid (see Analysis of Bronzes, below). The tin is left behind as metastannic acid, insoluble in dilute nitric acid, and the antimony is precipitated completely if ten times as much tin is present. In the presence of sufficient tin, all phosphorus and arsenic are also found in the insoluble residue as P_2O_5 and As_2O_5. The small quantity of the latter (and the remaining metals of this group) can be precipitated by hydrogen sulfide and separated from the copper group by means of alkaline sulfide solution (see *b*).

(*d*) *The Metals Occur as Insoluble Compounds.* — Fuse the substance with 6 parts of sodium carbonate and sulfur mixture, etc., as directed on p. 224.

For the determination of antimony in lead sulfate, etc., dissolve the lead salt in excess of potassium hydroxide, and pour the liquid into hot potassium sulfide solution (see *a*).

Analysis of Bronzes

Bronze is an alloy of tin and copper in varying proportions. It is likely to contain lead, aluminum, iron, manganese, zinc, and phosphorus. A good method for determining tin, copper, and lead in bronze has already been given (p. 223).

Procedure. — Place 0.5–1 g of the alloy borings† in a beaker, cover with 6 ml of nitric acid, *d.* 1.5,‡ add 3 ml of water, and cover the beaker

* Biltz, *Z. anal. Chem.*, **81**, 81 (1930).

† The borings are usually somewhat oily, in which case they should be washed with ether that has been distilled over potash, dried at about 80° C, and weighed after cooling in a desiccator. The washing with ether is best accomplished in a Soxhlet's fat-extraction apparatus, as shown in Fig. 54. Place the borings in the extraction-tube, and fill it with ether nearly up to the bend *b* of the siphon-arm. Connect the tube with the condenser *K*. After this add 20 to 30 ml of ether to the flask and heat gently on the water-bath. The ether vapors pass through the wide side-arm to the condenser *K*, where they are condensed and drop upon the borings. As soon as the ether in the tube has reached the height *b*, it is siphoned back into the flask, where it is again distilled. All the oil will be removed from the borings in from half an hour to an hour.

‡ Cf. p. 223.

with a watch glass. When the reaction begins to diminish, heat the liquid to boiling, until no more brown fumes are evolved, add 50 ml of boiling water, and keep the solution hot for at least 2 hours. Allow the precipitate (containing all the tin, the phosphoric acid, and always small amounts of copper oxide) to settle. Filter, wash with hot water, ignite in an open porcelain crucible, and weigh. In this way the weight of the $SnO_2 + P_2O_5 +$ foreign oxide is obtained. To obtain the weight of foreign oxide (chiefly copper oxide), fuse the precipitate with a mixture of sodium carbonate and sulfur as described on p. 224. Filter off the sulfides remaining after the solution of the melt in hot water, and convert into oxides by ignition in the air and weigh. By subtracting this weight from that previously obtained, the weight of $SnO_2 + P_2O_5$ is obtained. To obtain the weight of the SnO_2 analyze a separate portion for phosphoric acid (see below), and subtract the weight of phosphoric anhydride from the weight of $SnO_2 + P_2O_5$.

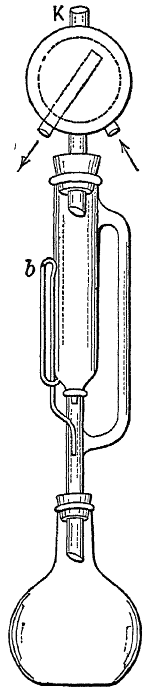

FIG. 54.

Dissolve the oxides obtained by the ignition of the insoluble sulfides in a little nitric acid (if Fe_2O_3 is present a little hydrochloric acid is also necessary) and add the solution of the nitrates to the first filtrate from the impure metastannic acid. To this solution add an excess of dilute sulfuric acid and evaporate on the water-bath as far as possible. Then heat over a free flame until dense, white fumes of sulfuric acid are evolved. After cooling, add 50 ml of water and 20 ml of alcohol, filter off the precipitate of lead sulfate and determine its weight as described on p. 186. Heat the filtrate from the lead sulfate to remove the alcohol, precipitate copper by means of hydrogen sulfide, and weigh as Cu_2S according to p. 193. In the filtrate from the copper sulfide the iron, aluminum, and zinc (also manganese) will be found. Evaporate to a small volume in order to expel the hydrogen sulfide, oxidize by the addition of concentrated nitric acid, and separate the iron and aluminum from zinc by means of a double precipitation with ammonia,* whereby the iron and aluminum are left behind as hydroxides

* If considerable zinc is present, the above separation is inexact. In this case treat the filtrate from the copper sulfide with sodium acetate, heat to 60°, saturate with hydrogen sulfide, and determine iron and aluminum in the filtrate, and zinc in the precipitate. If manganese is present in the alloy, separate it from iron and aluminum as described on pp. 158–163.

and are analyzed according to p. 114. Precipitate the zinc in the filtrate, after acidifying with acetic acid, by passing hydrogen sulfide into the boiling solution. Filter off the precipitated zinc sulfide, dissolve in hydrochloric acid, evaporate to dryness in a weighed platinum dish, and transform to oxide by heating with mercuric oxide by Volhard's method (cf. p. 148).

For the phosphorus determination Oettel* recommends the following procedure: Dissolve 2–5 g of the substance, as before, in nitric acid, filter off the impure metastannic acid with all the phosphorus, dry, and transfer as completely as possible to a porcelain crucible. Add the ash of the filter and ignite the contents of the crucible. After cooling, mix the substance with three times as much solid potassium cyanide, cover the crucible, and fuse the contents; the stannic oxide is reduced to metal, $SnO_2 + 2\,KCN = 2\,KCNO + Sn$, while the phosphoric acid is converted into potassium phosphate.

By skilfully rotating the crucible during the fusion, it is possible to unite the small particles of molten tin into a larger button whereby the subsequent filtration is greatly facilitated. After cooling, treat the melt with water and filter. Under a good hood, cautiously add hydrochloric acid to the filtrate and boil to remove the hydrocyanic acid. Then saturate with hydrogen sulfide to precipitate small quantities of copper and tin which are likely to be present. Free the filtrate from hydrogen sulfide by boiling, make ammoniacal, and precipitate the phosphoric acid as magnesium ammonium phosphate by the addition of magnesia mixture. After standing for 12 hours, filter off, wash with $1.5\,N$ ammonia water, dry, ignite and weigh as $Mg_2P_2O_7$.

Ordinary bronzes may be analyzed satisfactorily in the following manner: Treat the alloy with nitric acid as described above, remove the metastannic acid by filtration and electrolyze the filtrate, using a dull platinum dish as cathode and a plate as anode, both of which are weighed. Carry out the electrolysis with a current of 1 to 1.2 amperes at about 60°, and at the end of $2\frac{1}{2}$ to 3 hours wash the electrodes without breaking the circuit. On the anode will be found all the lead as PbO_2 and on the cathode will be found the copper. The siphoned solution contains the iron, aluminum and zinc, which are determined as above. Determine the phosphorus in another sample.

Remark. — The method just outlined will give exact results only when the metastannic acid is purified and the recovered solution of copper and lead nitrates added to the main solution. In the electrolysis, the chief dangers to be feared are having the solution so acid that the copper is not all precipitated, or so dilute that a spongy deposit is obtained.

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* *Chem. Ztg.*, **1896**, 19.

For the phosphorus determination Lundell and Hoffman* proceed as follows:

Weigh out 1–3 g of sample into a 300-ml Erlenmeyer flask and dissolve in 20 ml of aqua regia. When all the metal has dissolved add 10 ml of water and digest at 90° for 10 minutes. Dilute to 50 ml and treat with 100 ml of ammonium molybdate solution prepared as recommended by Blair (see Index).

Stopper the flask with a rubber stopper and shake for 10 minutes, occasionally removing the stopper. Allow to stand 4 hours or longer before filtering. Filter, keeping as much as possible of the precipitate in the flask. Wash the precipitate 5 times by decantation with 10-ml portions of 1 per cent nitric acid.

Dissolve the precipitate on the filter in $5N$ ammonium hydroxide containing 0.5 g of citric acid. Pour this on the filter in small portions, and catch the filtrate in the original flask containing the bulk of the precipitate. Do not use more than 50 ml of the ammonium hydroxide. Warm the solution slightly to dissolve the precipitate, replace under the funnel, and wash the filter with a little hot 5 per cent hydrochloric acid. If the ammoniacal filtrate is not clear at this stage, filter through the same filter and wash the filter with hot water.

Make the solution acid with hydrochloric acid, and without regard to a slight precipitate of molybdic acid, which, however, seldom forms in the analysis of alloys with low phosphorus, add 20 ml of magnesia mixture (p. 209). Heat to boiling and slowly add ammonium hydroxide till a precipitate forms or the solution is ammoniacal. Finally add enough $15N$ ammonium hydroxide to make the solution $1.5N$ with ammonia and allow to stand 4 hours. Filter, wash with cold $1.5N$ ammonium hydroxide and finish the analysis as described on p. 81.

SEPARATION OF THE THIO-ACIDS FROM ONE ANOTHER

Arsenic from Antimony

For separating arsenic from other elements one of the following properties can be utilized: (1) Arsenic pentasulfide is less soluble than most other sulfides and can be formed by introducing hydrogen sulfide into a cold solution containing quinquevalent arsenic which has been made strongly acid by adding considerable concentrated hydrochloric acid. (2) Arsenic trichloride is easily volatilized from solutions containing trivalent arsenic and hydrochloric acid. (3) Arsenic in the quinquevalent state forms characteristic precipitates of $MgNH_4AsO_4 \cdot 6H_2O$ and of Ag_3AsO_4.

The volatility of $AsCl_3$ is the basis upon which the best methods of separating arsenic from other elements rest. This volatility must also be borne in mind in all work with arsenic compounds, and solutions of quinquevalent arsenic should not be

* *Ind. Eng. Chem.*, **15**, 172 (1923).

boiled long with hydrochloric acid as there is danger of some arsenic trichloride being formed. Germanium is the only other element likely to be volatilized with the $AsCl_3$ under the conditions recommended for the analysis, and in those rare cases where germanium is present, it can be volatilized as $GeCl_4$ in a stream of chlorine; later the arsenic can be reduced and distilled off in a stream of hydrogen chloride gas.

(a) *Volatilization Method of E. Fischer**

Principle. — This separation depends upon the ready volatility of arsenic trichloride in a current of hot hydrochloric acid gas, under which conditions antimony chloride is not volatile if the temperature is kept below 105°. If the arsenic is present as arsenic acid, as is usual, the distillation must take place in the presence of some reducing agent.†

Procedure. — Use an apparatus similar to that shown in Fig. 55 for this determination. In the course of analysis, the arsenic and antimony, as a rule, are obtained first as sulfides, and these should be dissolved in caustic potash solution and oxidized by chlorine. Instead of using

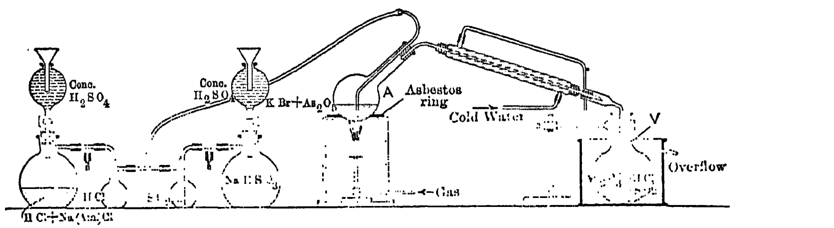

FIG. 55.

chlorine, the alkaline solution may be boiled with hydrogen peroxide or potassium percarbonate. If this method is used for the oxidation, the boiling must be continued until there is no further evolution of oxygen.

Transfer the oxidized solution, by means of a long-stemmed funnel, to the 500-ml distilling flask, *A*, in which has been placed 1.5 g of potassium bromide.‡ Dilute the solution in the flask with 12 *N* hydro-

* *Z. anal. Chem.*, **21**, 266. The process as described in the modification of M. Rohmer, *Ber.*, **34**, 33 and 1565 (1901).

† Fischer used a ferrous salt, O. Piloty and A. Stock used hydrogen sulfide (*Ber.*, **30**, 1649), and Friedheim and Michaelis used methyl alcohol (*Ber.*, **28**, 1414).

‡ Instead of the potassium bromide, hydrogen bromide may be used which has previously been prepared by treating 1 g of bromine with sulfurous acid. It is not permissible to introduce the bromine into the flask, *A*, and convert it there to hydrogen bromide by introducing sulfur dioxide gas into the flask, because it is then possible for bromine vapors to get into the receiver by means of the air which is first expelled from the apparatus, and the bromine would oxidize the volatilized $AsCl_3$, and thus interfere with the subsequent determination of the arsenic by precipitation as the trisulfide, or by titration.

chloric acid to a volume of about 200 ml. The receiver, *V*, consists of a large flask of 1.5–2 liter capacity; keep it cold by circulating a stream of cold water. At the start place 800 ml of cold water in the beaker, and during the analysis keep cold water running through the condenser and have it overflow into the beaker containing the receiving flask. With the apparatus all connected as shown in the drawing, heat the distilling flask and distil in a current of hydrogen chloride,* meanwhile constantly passing a little sulfur dioxide into the flask. At the end of about 45 minutes, when the volume of liquid in *A* is reduced to about 40 ml, remove the flame and disconnect the T-tube between the two evolution flasks in order to prevent liquid from backing up into the wash-bottles. Rinse off the adapter tube which connects the condenser with the receiver and remove the receiver.

Place another receiver at the end of the apparatus and make a second distillation to make sure that all the arsenic has been volatilized.† Then, for the determination of the arsenic, dilute the contents of the two receivers with hot water to a volume of about 1250 ml, and remove the excess of sulfurous acid by heating to boiling and passing a stream

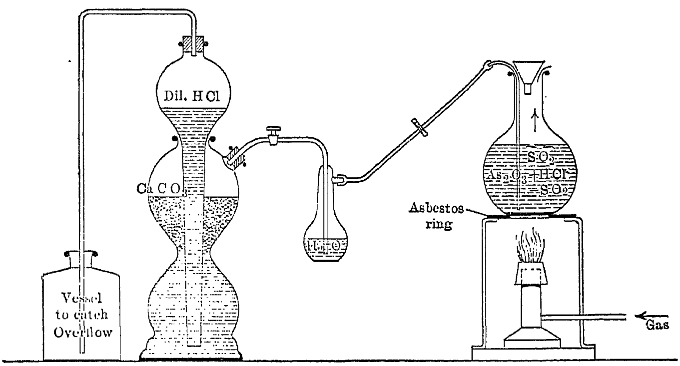

FIG. 56.

of carbon dioxide through the liquid as is shown in Fig. 56. When all the sulfur dioxide has been expelled (as can be shown by inserting a stopper with delivery tube into the flask so that the escaping vapors can be led into a dilute sulfuric acid solution of decinormal permanganate which will be decolorized by sulfur dioxide), allow the solution to cool

* If there is any tendency to suck back, a little more sulfur dioxide should be introduced.

† Rohmer found that as much as 0.15 g arsenic was volatilized completely by one distillation.

and determine the arsenic as trisulfide according to the directions on p. 208, or titrate the arsenic with iodine.

To accomplish the titration, add 3 drops of phenolphthalein indicator solution to the solution and add solid potassium hydroxide until a permanent pink color is imparted to the liquid. Then decolorize the solution by a few drops of hydrochloric acid, add 5 g of sodium bicarbonate, and titrate with decinormal iodine solution as described in Part II.*

Determine the antimony by treating the contents of the distilling flask with 2 or 3 g of tartaric acid, washing the solution into an Erlenmeyer flask, expelling the sulfur dioxide as above,† and determining the antimony gravimetrically by precipitating as the trisulfide according to the directions on p. 218, or volumetrically by titration with iodine as described in Part II.

Determination of Arsenic in Commercial Sulfuric Acid

To about 30 ml of concentrated hydrochloric acid and a little potassium bromide, or hydrogen bromide in the distilling flask *A* (Fig. 55), add 50–100 g of the acid to be tested (determine the weight by weighing a flask before and after adding the acid) through a funnel that is fastened by means of rubber tubing to the upper end of the delivery tube which enters the flask.‡ Rinse out the funnel with concentrated hydrochloric acid, and begin distilling.

When the contents of the distilling flask have been concentrated so that only the original volume of the concentrated sulfuric acid remains, keep the acid hot by means of a small flame until all the arsenic has been expelled. On account of the high temperature, 1 g of arsenic will be driven over in about 15 minutes. Finish the analysis as described above.

(*b*) *Precipitation of* As_2S_5

The precipitation of As_2S_5 from strong hydrochloric acid solutions was described on p. 209.

Procedure. — Starting with a precipitate consisting of the trisulfides of arsenic and antimony, dissolve this in caustic potash solution and

* A blank determination should be made with all the reagents that are used, and the iodine solution must be standardized in a solution as dilute as that in which the analysis is made.

† The escaping gas will not decolorize a solution of 2–3 ml dilute sulfuric acid and one drop of 0.01 *N* $KMnO_4$, when all the SO_2 is expelled.

‡ When the concentrated sulfuric acid runs into the flask, it often happens that distillation begins, and some of the arsenic would be lost if the flask, *A*, were left open.

oxidize exactly as described under the previous method. To the solution add acid, wash the acid solution into an Erlenmeyer flask and cool by surrounding the flask with ice. In another flask likewise cool some $12N$ hydrochloric acid. When both solutions are at 0°, dilute the arsenic-antimony solution with twice its volume of concentrated hydrochloric acid. Into this cold solution pass a rapid stream of hydrogen sulfide for 90 minutes. Stopper the flask and allow to stand an hour or more before filtering off the As_2S_5 through a Gooch crucible. Wash the precipitate with $4N$ hydrochloric acid until 1 ml of the filtrate after being considerably diluted with water and tested with hydrogen sulfide shows no precipitation. Then wash with water and finally with hot alcohol. After drying at 110° C, weigh the precipitate as As_2S_5.

Dilute the filtrate from the arsenic sulfide with about four times as much water and saturate with hydrogen sulfide. Filter off the Sb_2S_5 into a Gooch crucible, dry at 280° C in a current of carbon dioxide, and weigh as Sb_2S_3 (p. 218).

(c) *Precipitation o*

Principle. — The separation is based upon the fact that, if magnesia mixture is added to a solution of an alkali arsenate and antimonate containing tartaric acid, only arsenic will be precipitated.

Procedure. — Oxidize the solution obtained by dissolving the sulfides in aqueous caustic potash as described under (*a*). Make acid with hydrochloric acid and add 3 g of tartaric acid. Add an excess of ammonia; if a precipitate forms, it shows that an insufficient amount of tartaric acid is present. In this case decant off the clear solution, dissolve the precipitate by warming with tartaric acid, and mix the two solutions. To the clear, ammoniacal solution, add magnesia mixture (cf. p. 209, footnote) slowly with constant stirring. After standing 12 hours, filter off the precipitate of magnesium ammonium arsenate (it usually contains a little basic magnesium tartrate), and wash a few times with $1.5N$ ammonia. Dissolve the precipitate in hydrochloric acid, heat to boiling, and reprecipitate by the addition of an excess of ammonia. After standing for 12 hours more, filter off the precipitate, wash with $1.5N$ ammonia, and weigh as magnesium pyroarsenate as described on p. 210.

Remark. — Arsenic can also be separated from tin according to the above method, except that more tartaric acid is necessary to prevent the precipitation of the tin than when antimony alone is present (cf. p. 247).

(*d*) *Precipitation as A*

Transfer the sulfides of antimony and arsenic to a platinum dish and dissolve in a little fuming nitric acid. Evaporate off most of the excess acid; add 2 ml of 45 per cent hydrofluoric acid and a little water. Heat until a clear solution is obtained, and dilute to 100 ml. Cover with a quartz glass, heat just to boiling, and treat with 5 g of $K_2S_2O_8$ added cautiously in small portions. Cool, add a little methyl orange indicator solution, and make neutral with ammonia. Heat to boiling and add a slight excess of silver nitrate solution. Cool, filter off the chocolate-brown Ag_3AsO_4 precipitate, and wash it with water containing 5 g of NH_4NO_3 and 0.25 g $AgNO_3$ per liter. Finally wash with a little alcohol. Test the filtrate with more silver nitrate and make sure that it is neutral to litmus. Determine the silver content of the precipitate either gravimetrically as chloride or volumetrically by the Volhard method. In either case dissolve the precipitate in a little dilute nitric acid.

Separation of Antimony from Tin

(*a*) *F. W. Clarke's Method,*† *Modified*

Of all the known methods for the separation of antimony from tin, this is probably the most accurate. It depends upon the fact that antimony is completely precipitated from a solution containing oxalic acid, while stannic tin is not. Stannous sulfide, however, is decomposed by oxalic acid, forming an insoluble crystalline stannous oxalate, so that the tin must be in the stannic form.

Procedure. — In most cases it is a question of separating antimony from tin after these metals have been separated from the members of the copper group by means of alkali polysulfide; *i.e.*, the tin and the antimony are in the form of their soluble thio-salts.

To the solution of the thio-salts in a 500-ml beaker containing not more than 0.3 g of the two metals, add an aqueous solution of 6 g of the purest caustic potash (one-third the sum of the weights of tartaric and oxalic acids to be added) and 3 g of tartaric acid (ten times the maximum weight of the two metals). To this mixture slowly add perhydrol until the yellow solution is completely decolorized; then add 1 ml in excess and boil the solution for a few minutes to change any thiosulfate to sulfate and to decompose the greater part of the excess peroxide. As soon as the evolution of oxygen ceases, cool the solution somewhat, cover the beaker with a watch glass, and cautiously add a hot solution of 15 g pure recrystallized oxalic acid (5 g for 0.1 g of

* L. W. McKay. *J. Am. Chem. Soc.*, **50**, 368 (1928).

† *Chem. News*, **21**, 124. Cf. also Rössing, *Z. anal. Chem.*, **41**, 1. F. Henz, *Z. anorg. Chem.*, **37**, 18 (1903). Vortmann and Metzl, *Z. anal. Chem.*, **44**, 525 (1905).

the mixed metals). This causes the evolution of considerable gas ($CO_2 + O_2$). Now, in order to remove all the excess hydrogen peroxide, boil the solution vigorously for 10 minutes. The volume of the liquid should amount to 80–100 ml. After this, introduce a rapid stream of hydrogen sulfide into the boiling solution; for some time there will be no precipitation, but only a white turbidity formed. After 5 or 10 minutes the solution becomes orange-colored and the antimony begins to precipitate; from this point take the time. At the end of 15 minutes dilute the solution with hot water to a volume of 250 ml, at the end of another 15 minutes remove the flame; and 10 minutes later stop the current of hydrogen sulfide. Filter off the precipitated antimony pentasulfide through a Gooch crucible which, before weighing and after drying, has been heated in a stream of carbon dioxide at 300° for at least 1 hour. Wash the precipitate twice by decantation with 1 per cent oxalic acid and twice with very dilute acetic acid before bringing it in the crucible. Both of these wash liquids should be boiling hot and saturated with hydrogen sulfide. Weigh the Sb_2S_3 after the treatment described on p. 218.

To determine the tin, evaporate the filtrate to a volume of about 150 ml, nearly neutralize the excess of oxalic acid with potassium hydroxide, and deposit the tin electrolytically as described on p. 227.

According to Vortmann and Metzl,* antimony may be separated from tin by passing hydrogen sulfide into a solution containing hydrochloric and phosphoric acids of the proper concentration.

(b) *Method of H. Rose*

Principle. — This method is based upon the insolubility of sodium metantimonate and the solubility of sodium stannate in dilute alcohol.

Procedure. — Both metals are assumed to be present in the form of an alloy. Treat the alloy with nitric acid as already described (cf. pp. 223 and 230). Filter off the residue, wash with ammonium nitrate water, dry and transfer as completely as possible to a large silver crucible. Add the ash of the filter, and gently ignite the precipitate. Fuse the oxides with 10–12 times as much solid sodium hydroxide and a little sodium nitrate, or sodium peroxide, placing the silver crucible within a larger porcelain one in order to protect it from the flame. Keep the contents of the crucible liquid for 20 minutes. Cool, place the crucible in a large porcelain dish, and treat its contents with hot water until the melt has disintegrated, leaving the insoluble part in the form of a fine meal. Now add one-third of the solution's volume of

* *Z. anal. Chem.*, **44**, 533 (1905).

alcohol and stir the mixture well. Filter after standing 12 hours. Wash the residue remaining on the sides of the dish onto the filter with dilute alcohol (1 vol. alcohol + 2 vols. water). Wash the sodium metantimonate precipitate with diluted alcohol containing a few drops of sodium carbonate solution as follows: First with a mixture of 1 vol. alcohol + 2 vols. water, then with 1 vol. alcohol + 1 vol. water, and finally with 3 vols. alcohol + 1 vol. water. Continue washing until the filtrate when acidified with hydrochloric acid and tested with hydrogen sulfide no longer gives a yellow coloration (tin sulfide).

If considerable tin and little antimony were originally present, a single fusion of the oxides with caustic soda does not afford a complete separation, as the residue of sodium metantimonate always contains some tin. Dry the precipitate, therefore, separate it from the filter, and place in a silver crucible. Treat the filter repeatedly in a *porcelain* crucible with fuming nitric acid until the paper is completely destroyed and then remove the excess of acid by heating in an air-bath. Dissolve the contents of the porcelain crucible in a little caustic soda solution and wash into the silver crucible. Remove the water by heating the silver crucible at first on the water-bath and finally in an air-bath; add 10 g of solid caustic soda. Fuse the mixture and treat the melt in the same way as before.

The second residue of sodium metantimonate is free from tin. Dissolve it off the filter by a mixture of equal volumes 2.5 N hydrochloric and 7.5 per cent tartaric acids, in which it is readily soluble. From this solution precipitate the antimony by hydrogen sulfide and determine as described on p. 218. For the tin determination, gently heat the alcoholic filtrate to remove the alcohol, acidify slightly with hydrochloric acid, and precipitate the tin as sulfide by hydrogen sulfide and determine according to p. 226, β.

Remark. — If the oxide residue which was first fused with sodium hydroxide and nitrate consisted solely of tin and antimony oxides, this method gives very good results. As a rule, however, most antimony and tin alloys contain lead and other metals whose oxides remain to some extent with the tin and antimony on treatment of the alloy with nitric acid, so that the sodium metantimonate is subsequently rendered impure by the presence of these metals. The antimony determination therefore gives too high results. In this case the method of W. Hampe* should be used.

Dissolve the alloy in aqua regia (as described below in the analysis of bearing metal) and separate the tin and antimony from the remaining metals by means of colorless sodium sulfide. From the solution of the thio-salts precipitate the tin and antimony by making barely acid

* *Chem. Ztg.*, **18**, 1900.

with dilute sulfuric acid. Wash the precipitate and dissolve in a little warm sodium sulfide solution. After cooling, add sodium peroxide in small amounts to the concentrated solution until the liquid becomes colorless, and when treated with more sodium peroxide a distinct evolution of oxygen takes place. By this treatment sodium antimonate is formed; this separates out to some extent, but the tin remains in solution. To precipitate the antimony from the solution completely, add one-third as much alcohol, filter off the precipitate, and treat as above described.

Analysis of Bearing Metal

This alloy contains tin, antimony, lead, a little copper, and usually small amounts of iron, bismuth, and zinc.

Treat 1 g of thin borings in a small beaker with about 15 ml of 12 *N* hydrochloric acid to which 3 ml of concentrated nitric acid has been added. Add the acid slowly, a few drops at a time. If the alloy is rich in lead it is necessary to heat on the water-bath for some time, replacing the acid lost by evaporation. When the metal has dissolved, dilute the solution (it should be yellow, or greenish yellow if much copper is present) with 15 times as much alcohol, added in small portions with constant stirring. This stirring is indispensable because lead chloride separates out very slowly from a supersaturated alcoholic solution containing other chlorides. The complete precipitation is best recognized by the fact that no mark is left upon the sides of the beaker when the stirring-rod is rubbed against it.

After standing for 12 hours, with frequent stirring, filter off the precipitated lead chloride into a weighed Gooch crucible, wash with alcohol, dry at 150°, and weigh. In the filtrate will be found a few milligrams of lead in the presence of antimony, tin, copper, bismuth, iron, and zinc.* Pour the alcoholic filtrate into a large, deep porcelain dish† and evaporate off the alcohol at as low a temperature as possible. It is necessary to avoid evaporating the solution to dryness as in that case some $SnCl_4$ will be volatilized. When the alcohol is all gone, add 0.1 g of potassium chlorate, evaporate the solution to a small volume, add 1 g of tartaric acid and enough caustic potash to make the solution barely alkaline. Now add, dropwise, as recom-

* Alloys low in lead are not treated with alcohol in this way. It is best to decompose such alloys with chlorine gas, as described in the analysis of tetrahedrite (see Index), or to proceed as in the analysis of bronze, p. 230.

† In evaporating off the alcohol there is a tendency for the solution to creep over the edges of the dish so that it is advisable to employ a deep dish and to evaporate the liquid in small portions.

mended by Finkener, freshly prepared hydrogen sulfide water until no further precipitation takes place. In this way all the Cu, Bi, Fe, Zn, and the last of the Pb are precipitated as sulfides (precipitate *a*) while all the Sn and Sb remain in solution (solution *b*).*

Treatment of Precipitate a

Filter off the precipitate, wash with hydrogen sulfide water, dissolve in $6N$ nitric acid and evaporate with hydrochloric acid to remove the nitric acid. Dilute the solution of chlorides until it is only $0.3N$ in acid. Precipitate the Cu, Pb, and Bi as sulfides by hydrogen sulfide, filter, and wash with water containing H_2S. The filtrate contains the iron and zinc (filtrate *c*).

Dissolve this last precipitate in nitric acid, evaporate with the addition of 4 or 5 drops of concentrated sulfuric acid, and determine the last of the lead as sulfate according to p. 186. From this filtrate precipitate bismuth with an excess of ammonia and determine as Bi_2O_3 according to p. 191.

In the ammoniacal filtrate from the bismuth precipitation, determine the copper electrolytically, after acidifying with sulfuric acid, according to p. 195, or as cuprous sulfide, according to p. 193.

To determine the iron and zinc, oxidize the *filtrate c* by boiling with a little concentrated HNO_3, precipitate the iron by an excess of ammonia, and weigh as Fe_2O_3, p. 99. Determine the zinc in this last filtrate by acidifying with acetic acid, precipitating as sulfide and weighing as such, according to p. 150.

Treatment of Solution b

To determine the antimony and tin, dilute the alkaline solution to exactly 250 ml in a measuring-flask, and after thoroughly mixing, withdraw 100 ml in a pipet, transfer to a 400-ml beaker, acidify with acetic acid, and boil to expel the hydrogen sulfide. Then add 3 g of tartaric acid and 6 g of purest potassium hydroxide, whereby any precipitated sulfide is redissolved. At this point add perhydrol as described on p. 238, and separate the antimony and tin.

Alternate Method for the Analysis of Bearing Metal

The above method is that given in the German edition of this book. It will give good results. In the United States it is common practice to carry out the analysis somewhat differently. The following procedure is similar to that recommended by

* The separation is complete only when all the tin is in the quadrivalent condition. In driving off the alcohol there is always some stannous chloride formed which must be subsequently oxidized by means of $KClO_3$ and HCl.

the Bureau of Standards at Washington, D. C. The Bureau furnishes for practice analysis two samples of bearing metal each of which has been analyzed by at least ten independent laboratories. One sample contains about 79 per cent lead, 11 per cent tin, 10 per cent antimony, and less than 0.2 per cent of bismuth, copper, and iron. The other contains 88 per cent tin, 7.3 per cent antimony, 3.8 per cent copper, 0.56 per cent lead, and small quantities of iron, bismuth, and arsenic.

Determination of Lead, Bismuth, Copper, and Iron. — Weigh out 2-g portions of finely cut alloy into 300-ml Erlenmeyer flasks. Treat with a mixture of 20 ml 12 N hydrochloric acid and 4 ml concentrated HNO_3, adding the acid gradually in small portions. If the alloy is rich in lead, heat on the water-bath and replace the acid lost by evaporation. When all the metal has been acted upon, heat until oxides of nitrogen are expelled, add 10 ml of 20 per cent tartaric acid solution, and dilute to about 300 ml. Heat to dissolve lead chloride, make alkaline with sodium or potassium hydroxide, and add about 2 g of hydroxide in excess. Introduce a rapid stream of hydrogen sulfide for 15 minutes. In this way all the lead, bismuth, copper, and iron are precipitated as sulfides while the tin, antimony, and arsenic remain in solution as thiosalts. Digest on the hot plate or steam-bath for at least an hour. Filter and wash the residue with a 2 per cent solution of alkali sulfide. Discard the filtrate.

Transfer the sulfide precipitate back to the original flask. To remove the last traces of sulfide from the paper, place the flask under the funnel containing the paper, and pour 10 ml of concentrated nitric acid along the upper edge of the paper. After the acid has stopped running, wash with a little hot water. Heat the contents of the flask until practically all the sulfide is dissolved. Then replace the flask under the filter again and pour 10 ml of bromine water along the upper edge of the filter. Wash the filter again with hot water and make sure that no residual sulfide remains under the fold. Use more nitric acid and bromine if necessary. To the nitric acid solution of the sulfides, add 15 ml of 18 N sulfuric acid and evaporate to strong fumes. Make sure that all the nitric acid is expelled. Cool, dilute with 100 ml of cold water and heat to boiling. Cool, filter into a weighed Gooch crucible that has been heated to about 400°, and wash four times with cold 8 per cent sulfuric acid and finally with a little cold water. Dry at 105° and then heat to about 400° by placing the crucible inside a slightly larger one without a solid bottom, and heating over a Tirrill burner. Weigh as $PbSO_4$.

Dilute the filtrate to about 500 ml and partially neutralize by adding 10 ml of concentrated ammonium hydroxide. Heat nearly to boiling,

saturate the hot solution with hydrogen sulfide, filter off any precipitate that may form, and wash with hydrogen sulfide water.

Dissolve the precipitated sulfides of copper and bismuth in 10 ml of hot, $3N$ nitric acid and filter off residual sulfur if necessary. Precipitate the bismuth as hydroxide by adding ammonium hydroxide, and determine as phosphate according to p. 190. Determine the copper by electrolysis as described on p. 195.

Determination of Arsenic. — Digest 5 g of the fine borings with 25 ml of concentrated sulfuric acid until the metal has been completely attacked. Cool and dilute carefully with 50 ml of water. Cool to room temperature and transfer with the aid of 150 ml of concentrated hydrochloric acid to a distilling flask. Add 10 g of cuprous chloride, or ferrous sulfate, and distil off about 100 ml of the mixture. Use an upright condenser, and in the outlet tube make a small hole on the side just below the stopper so that the exit of the gas will not be impeded by drops of liquid collecting at the bottom of the condenser tube. Catch the distillate in 150 cc of ice-water, the end of the tubing from the condenser dipping below the surface of the water. When 75 ml of distillate have been collected, remove the flame, add 15 ml of hypophosphorous acid and 20 ml of concentrated hydrochloric acid to the remaining contents of the distilling flask, and distil off 15 ml more. This causes the distillation of all the arsenic as $AsCl_3$.

After the distillation is completed, partially neutralize the acid in the distillate by adding 15 ml of concentrated ammonium hydroxide and introduce a rapid stream of hydrogen sulfide. Filter off the arsenic trisulfide precipitate and wash with hot water till all chloride is removed. Dissolve the arsenic trisulfide in 2–3 ml of concentrated ammonium hydroxide, washing the filter with small portions of hot water directed toward the upper edge of the filter, using as little water as possible to effect thorough washing. Evaporate the solution nearly to dryness, add 10 ml of concentrated nitric acid, and again evaporate nearly to dryness. This causes oxidation of the arsenic to arsenate or arsenic acid. Take up in 100 ml of water, add 10 ml of $0.2N$ silver nitrate solution, and carefully add NH_4OH to barely alkaline reaction. Then add $6N$ HNO_3 dropwise until any precipitate of silver arsenate just dissolves or the solution is barely acid to litmus. It is important that the solution should be practically neutral. Then, on adding 10 ml of saturated ammonium or sodium acetate solution, all the arsenic will be precipitated as silver arsenate, Ag_3AsO_4. Heat to boiling, filter, and continue as described for the determination of arsenic in ores by the Low-Pearce-Bennett method.

Determination of Antimony. — Digest accurately weighed 0.4-g samples of alloy in 250-ml flasks with 12 ml of concentrated H_2SO_4 and about 5 g of $KHSO_4$. Heat over a free flame while constantly rotating the contents of the flask until the metal has all dissolved.

It is desired to get the antimony into solution as $Sb_2(SO_4)_3$ and the tin as $Sn(SO_4)_2$.

$$2\,Sb + 6\,H_2SO_4 = Sb_2(SO_4)_3 + 3\,SO_2 + 6\,H_2O$$
$$Sn + 4\,H_2SO_4 = Sn(SO_4)_2 + 2\,SO_2 + 4\,H_2O$$

If the alloy is heated too gently, sometimes a part of the tin is left in the stannous condition, and this is fatal to the analysis. The acid should be heated nearly to the boiling point to accomplish the second stage in the oxidation of the tin.

When the sample is completely decomposed and the sulfuric acid has fumed strongly for several minutes, allow to cool and then add very cautiously 5 ml of water. Follow this with 20 ml of 12 N hydrochloric acid and boil gently for 3 minutes. Cool, add 100 ml of cold water, and titrate at a temperature below 15° with 0.1 N permanganate. The end point should remain for 20 seconds if the above directions were followed. Save the solution for the tin determination.

According to Lundell,* the solution should contain 10 to 25 per cent of concentrated HCl by volume, and approximately 10 per cent by volume of concentrated H_2SO_4 is desirable. The above directions provide for 10 per cent of HCl and somewhat less than 6 per cent of H_2SO_4 by volume. The procedures recommended by the Bureau of Standards and by Lundell, Hoffman, and Bright call for less than 5 per cent H_2SO_4. The titration of antimony with permanganate gives very accurate results when the conditions are right, and this method of determining antimony is used more than any other in commercial testing. If the conditions are not right, the end point may be very hard to find. For many years chemists avoided as much as possible all titrations with permanganate in the presence of hydrochloric acid because hydrochloric acid is easily oxidized to chlorine or hypochlorous acid, a reaction which is catalyzed by the presence of other substances such as ferrous salt. By keeping the solution cold, by making sure that all tin, iron, etc., is oxidized by sufficiently long treatment with hot sulfuric acid, and by adding appropriate quantities of hydrochloric and sulfuric acids, this oxidation of HCl is prevented. The titration reaction can be expressed as follows:

$$5\,Sb^{+++} + 2\,MnO_4^- + 16\,H^+ = 5\,Sb^{+++++} + 2\,Mn^{++} + 8\,H_2O$$

and the milli-equivalent of antimony is 0.06088 g.

Determination of Tin. — Transfer the titrated solution from the antimony determination to a 500-ml Erlenmeyer flask; add 65 ml more of concentrated hydrochloric acid and about 2 g. of test lead powder. Stopper the flask with a rubber stopper carrying a long glass tube which extends from the bottom of the stopper upward for about an inch and then bends downward through a wide arc to a point on the outside

* *Applied Inorganic Analysis*, p. 228.

nearly level with the bottom of the flask when the stopper is inserted. Heat the contents of the flask to boiling and boil gently for 30 minutes. Then remove the flame and, without removing the stopper from the flask, insert the outer end of the tubing it carries into a beaker containing 200 ml of saturated $NaHCO_3$ solution (about 22 g of $NaHCO_3$). While keeping the tubing in this $NaHCO_3$ solution, cool the contents of the flask by cold, running water. Cool slowly at first. At the end of the reduction with lead,

$$Sn^{++++} + Pb = Sn^{++} + Pb^{++}$$

the flask is filled with steam; but as the contents cool and the steam condenses, the $NaHCO_3$ solution is sucked into the flask and CO_2 is formed which exerts a pressure and will force back the liquid in the tubing and perhaps bubble through the $NaHCO_3$ solution. In this way the flask becomes filled with CO_2 rather than air, of which the oxygen would oxidize some of the stannous ions back to the stannic state. Finally cool to about 10° (using ice-water or dry ice if necessary), add 5 ml of starch indicator solution, and titrate fairly rapidly with 0.1 *N* iodine solution.

Instead of using the above device for filling the flask with CO_2, a stream of CO_2 gas can be kept passing through the solution during the reduction with Pb and particularly during the cooling of the solution. Some chemists add a lump or two of calcite ($CaCO_3$) to the reduced solution which slowly dissolves in the acid with liberation of CO_2. If some dry ice is available, a little of it placed in another flask will furnish a convenient source of CO_2. On placing this flask in warm water, an abundant stream of CO_2 is evolved which can be led into the flask containing the solution of the alloy by means of tubing extending nearly to the bottom of the flask containing the solution that is being analyzed. The above scheme of sucking $NaHCO_3$ back into the solution works nearly as well. It has been recommended to add the iodine solution through tubing that runs through the stopper so that there is absolutely no chance for air to enter the flask during the titration. The titration of $SnCl_2$ with iodine is very accurate, but it is necessary to have all the tin in the stannous condition and to prevent any back oxidation by air, or the results of the analysis will be low. Various other reducing agents such as a coil of nickel wire, metallic iron, powdered antimony, etc., have been recommended instead of the test lead, but in every case the chief source of trouble is oxidation by the air.

Separation of Arsenic from Tin and Antimony

*(a) Method of Fred. Neher**

Dissolve the moist sulfides in freshly prepared ammonium sulfide, evaporate nearly to dryness in an Erlenmeyer flask, and oxidize with hydrochloric acid and potassium chlorate. From this solution precipi-

* *Z. anal. chem.* (1893), **32**, 45.

tate the arsenic as sulfide under the conditions described on p. 208. In the filtrate from the arsenic pentasulfide all the tin is found and can be precipitated as sulfide after diluting largely with water and passing in hydrogen sulfide. Ignite and change to the oxide as described on p. 226, β.

(b) *Method of W. Hampe**

Dissolve the precipitated sulfides, as soon as possible after filtering and washing, in freshly prepared ammonium sulfide, evaporate the solution nearly to dryness, and oxidize with hydrochloric acid and potassium chlorate in a flask connected with a return-flow condenser.† Add tartaric acid and ammonia, and precipitate the arsenic with magnesia mixture as magnesium ammonium arsenate, according to p. 209. After standing 12 hours, filter off the precipitate, wash with 1.5 N ammonia, and, in order to remove a little magnesia, dissolve the precipitate in hydrochloric acid and reprecipitate by the addition of ammonia. After standing another 12 hours, filter off the precipitate and again wash with 1.5 N ammonia.

This precipitate can be converted into magnesium pyroarsenate and weighed in this form as described on p. 210. The transformation is somewhat tiresome, however, so that Hampe prefers to dissolve the precipitate in hydrochloric acid once more, to precipitate the arsenic by means of hydrogen sulfide, and then to determine the magnesium in the evaporated filtrate as magnesium pyrophosphate according to p. 80 or p. 81.

(c) *Method of Plato-Hartmann*‡

In this interesting method the chlorides of arsenic, antimony, and tin, in the lower states of oxidation, are heated with a mixture of phosphoric and hydrochloric acids. Arsenous and antimonous chlorides distil by raising the temperature to 165°, but stannous chloride forms a complex with phosphoric acid and remains behind. According to Plato, tartaric acid is added to the first distillate and by a second distillation the arsenous chloride is removed. Hartmann prefers to precipitate the arsenic as trisulfide from a solution quite strongly acid and antimony as trisulfide in the partially neutralized filtrate. After the trichlorides of arsenic and antimony have been distilled from the solution containing hydrochloric and phosphoric acids, the tin is volatilized as stannic chloride by the addition of hydrobromic acid. The latter reacts with the hot, concentrated sulfuric acid and is to some extent oxidized into bromine which in turn oxidizes the tin to volatile stannic chloride.

For the distillations, the apparatus shown in Fig. 57 is suitable. On the extreme

* *Chem. Ztg.* (1894), **18**, p. 1900.

† So that no arsenic trichloride will be lost by volatilization.

‡ Plato, *Z. anorg. Chem.*, **68**, 26 (1911); *Z. anal. Chem.*, **50**, 641 (1911); Hartmann, *Z. anal. Chem.*, **58**, 148 (1919).

right of the drawing is shown a Kipp generator for producing carbon dioxide, connected through the wash-bottle and the long glass tube to B into which acid can be made to drop from the funnel T. The lower part of B leads almost to the bottom of the flask A. The stopper of the flask is also fitted with a thermometer and a gas exit tube D, leading to the condenser P, which in turn is connected with the receiver E, in which the subsequent precipitation can also take place. The uncondensed vapors pass through the tube K, containing glass beads wetted with water, into the tubing R, which is connected with the tower G containing pieces of marble. In this way the acid vapors are neutralized so as not to be obnoxious.

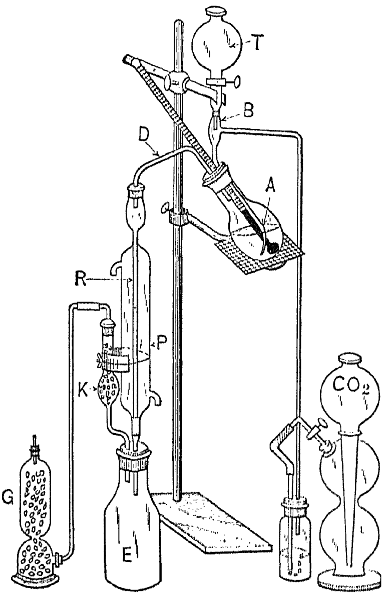

Fig. 57.

It is advisable to wind cord around D to prevent the vapors being cooled too much by the air; for the same reason the neck of the flask A should be covered with asbestos paper.

Procedure. — If the sample is an alloy, weigh out 1 g of the fine borings into the flask A, Fig. 57, add 6 ml of concentrated sulfuric acid, and heat until decomposition is complete. Of arsenic, antimony, and tin sulfides, place the precipitate and filter in the flask and add enough sulfuric acid so that the mass is not quite dry after the carbonization of the filter; continue heating until the sulfuric acid solution is colorless, or a light straw color, and volatilize any sulfur in the neck of the flask by heating carefully with a flame. Evaporate off the excess sulfuric acid, leaving about 6 ml in the flask. If the carbon of the filter is not oxidized sufficiently, there will be too much foaming during the subsequent distillation.

Cool, add 7 ml of aqueous phosphoric acid, *d.* 1.70, again cool, add 10 ml of concentrated hydrochloric acid, and connect the apparatus with a little water in the receiver. Introduce a slow stream of carbon dioxide, begin heating the flask, and cause concentrated hydrochloric acid to drop into the flask so that the volume of liquid in the flask does not change much during the distillation. Keep the temperature at 155–165°. The arsenic trichloride distils readily, but it may take 2 or 3 hours to distil all the antimony trichloride. To test for antimony, disconnect the receiver and collect about 20 drops of fresh distillate. To this add a little

hydrogen sulfide water and ammonia water to neutralize some of the acid; if no orange precipitate forms, antimony is absent.

When all the antimony has been volatilized as chloride, stop distilling and disconnect the receiver. Using a fresh receiver, continue the distillation using a mixture of one-fourth pure hydrobromic acid, *d.* 1.40, and three-fourths concentrated hydrochloric acid in the dropping-funnel. If bismuth is present, keep the temperature below 145°. Distil until no test for tin is obtained with 1 ml of distillate. A little sulfur dioxide is always present in the distillate, being formed by the interaction of hydrobromic and sulfuric acids. There is, therefore, always some sulfur precipitated when the H_2S water is added, but this milky turbidity can be distinguished from a precipitate of yellow stannic sulfide that forms more quickly. The distillation should not be stopped until there is no sign of yellow precipitate in the test.

To determine arsenic in the first distillate, introduce hydrogen sulfide and treat the precipitate of arsenic trisulfide as described on p. 208.

To determine antimony in the filtrate which contains hydrogen sulfide, neutralize with ammonium hydroxide until a permanent precipitate of orange antimony sulfide forms. Add a little more ammonium hydroxide, dilute with an equal volume of hot water, and saturate with hydrogen sulfide gas. Treat the antimony trisulfide precipitate as directed on p. 218.

To determine tin, take the second distillate, dilute with a little water and add ammonium hydroxide until the stannic hydroxide precipitate does not redissolve well on stirring. Saturate with hydrogen sulfide, allow to stand over night, and treat the precipitate as directed on p. 224. Added filter-paper pulp aids in filtering the stannic sulfide.

Separation of Antimony from Arsenic and Tin

(*a*) *Method of Rose*

Heat the sulfides of arsenic, antimony, and tin with fuming nitric acid in a large covered beaker until the sulfur is completely oxidized, and remove the excess of acid by evaporation on the water-bath. Treat the slightly moist residue with concentrated sodium hydroxide solution and transfer the contents of the dish to a silver crucible. Add a little solid sodium hydroxide, and dry the contents of the crucible in an air-bath. Place the silver crucible in a larger porcelain one, heat over a Méker or Teclu burner, and keep the contents of the smaller crucible liquid for about 20 minutes. Cool, extract the melt with water, add one-third as much alcohol to precipitate sodium metantimonate completely, and after standing 12 hours filter off the pre-

cipitate and subject it to the treatment described on p. 240. Make the filtrate containing all the arsenic and tin acid with hydrochloric acid, whereby stannic arsenate is precipitated. Without filtering, conduct hydrogen sulfide into the liquid, filter off the precipitated sulfides of tin and arsenic, oxidize with hydrochloric acid and potassium chlorate, and separate the arsenic from the tin as described on p. 234.

(*b*) *Method of Hampe*

Oxidize the moist sulfides as described on p. 242, *b*, and determine the arsenic in the same way.

In the combined filtrates from the magnesium ammonium arsenate precipitate the antimony and tin by hydrogen sulfide, after making the solution acid. Separate these according to one of the methods already described; cf. p. 238.

SUPPLEMENT TO THE HYDROGEN SULFIDE GROUP

GOLD, PLATINUM, SELENIUM, TELLURIUM, VANADIUM, MOLYBDENUM, TUNGSTEN

GOLD, Au. At. Wt. 197.2

Gold is always determined as the metal itself. There are three cases to distinguish:

1. The gold is present in solution.
2. The gold is alloyed with copper and silver.
3. The gold is present in an ore.

1. Gold is Present in Solution

Usually gold is deposited as metallic gold from its solutions and weighed after filtering and washing.

For the deposition of gold the following reducing agents can be used: ferrous sulfate, oxalic acid, formaldehyde, and hydrogen peroxide. If the gold is to be precipitated by means of either *ferrous sulfate* or *oxalic acid*, no free nitric acid can be present in the solution. If some is present, it must be removed by repeated evaporation with concentrated hydrochloric acid and the solution then diluted with water. To this dilute solution add a large excess of clear ferrous sulfate solution, cover the beaker, and heat its contents for several hours on the water-bath. Then filter off the precipitate, wash first with water containing hydrochloric acid until the iron is completely removed, and then with pure water. Dry the precipitate, transfer as completely as possible

to a porcelain crucible, add the ash of the filter, ignite, and weigh the gold. In this way gold can be separated from most metals, even platinum, but not from silver. If silver is present, as of course it never is in a dilute hydrochloric acid solution, remove it by the addition of hydrochloric acid, filter off the precipitated silver chloride, and treat the filtrate as above described.

To precipitate gold by means of *oxalic acid*, dilute the slightly acid solution with water, add an excess of oxalic acid, or ammonium oxalate with a little sulfuric acid, and allow the covered beaker to stand 48 hours in a warm place.

Filter off the yellow scales of deposited gold, and wash, as above described, with hydrochloric acid and then with water. Ignite and weigh.

*Precipitation of Gold by Means of Hydrogen Peroxide (L. Vanino and L. Seeman)**

If a gold solution is treated with caustic alkali solution and then with formaldehyde, or, better still, hydrogen peroxide, the gold is soon precipitated quantitatively, even in the cold. By boiling, the finely divided gold collects together and assumes a reddish brown color. The reaction takes place according to the following equation:

$$2\,AuCl_3 + 3\,H_2O_2 + 6\,KOH = 6\,KCl + 6\,H_2O + 3\,O_2 + 2\,Au$$

If the gold is deposited by this method from very dilute solutions it is obtained in such a finely divided condition that it passes through the filter. If, however, the solution is boiled until the excess of hydrogen peroxide is completely destroyed and it is then acidified with hydrochloric acid, the gold can be readily filtered. Gold can be separated from platinum by this method.

2. The Gold is Alloyed with Silver and Some Copper

Gold present in alloys is most rapidly and most accurately determined in the dry way. The principle of the method is very simple. Too much copper should not be present as high-copper alloys cannot be cupelled.

If a gold-silver alloy is melted in the air with lead upon a "cupel" (a very porous vessel made of bone-ash or magnesia) the lead and copper are oxidized, the oxides fuse and are absorbed by the cupel, while all the gold and silver are left behind in the form of a metallic button, which is weighed. The silver is afterwards separated from the gold

* *Ber.*, **32**, p. 1968 (1899).

by the action of nitric acid which dissolves the silver but leaves the gold behind. If the weight of the gold that is left undissolved is deducted from the weight of the gold-silver button the weight of the silver is obtained.

To obtain accurate results a number of precautions must be taken. By the cupellation of the alloy some noble metal is always lost and the amount lost increases in proportion to the amount of lead used and the higher the temperature. Furthermore, small amounts of the noble metal are absorbed by the cupel, and this loss is greater the smaller the quantity of lead used. This second loss amounts to much less than the former one occasioned by the use of too much lead. *Consequently, in every gold cupellation an unnecessary excess of lead must be avoided.*

Experience has shown that the richer a gold-silver alloy is in base metal the more lead is necessary for the cupellation. Furthermore, in the separation or *parting* of gold from silver by means of nitric acid, it is necessary to remember that the separation is quantitative only if the alloy consists of three or more parts of silver to one part of gold. If less than three parts of silver are originally present for one part of gold, it is necessary to add pure silver until this proportion is reached. This operation is known as *quartation* or *inquartation.* If a gold-silver alloy, in the form of foil, consisting of three parts of silver to one of gold, is treated with nitric acid, the gold remains behind as a brownish scale; if more silver is present, it is left as a fine powder, unless the acid is extremely dilute.

From what has been said, it is clear that accurate results can be obtained only when the correct amount of lead is present in the alloy that is cupelled, and when the gold and silver are present in the proper proportion; *i.e.*, it is necessary to know the approximate composition of the alloy before an accurate determination can be made. This is determined by

The Preliminary Assay

For this purpose heat a muffle, Fig. 58, to a cherry-red heat, place a cupel weighing from 6 to 7 g* in the back part of it, close the muffle door, and heat the cupel until it has acquired the same color as the muffle. Then place 5 g of lead upon the cupel, close the muffle until the lead is melted, and then, with the aid of tongs, drop into the molten lead 0.25 g of the accurately weighed alloy enveloped in a small piece of lead foil.

* A good cupel will absorb its own weight of litharge. During the cupellation about one-tenth of the litharge formed is lost by volatilization, so that the weight of litharge absorbed by the cupel is practically that of the original lead button. Figure 59 represents a cupel, together with its cross-section.

Close the muffle until the alloy has melted and shows a bright upper surface. With the help of an iron hook, carefully shove the cupel to about the middle of the muffle and leave the door open so that there is a ready access of air into the muffle.

After about 20 minutes all the lead will be absorbed, this condition being indicated by the "blick." The blick is the brightening of the metal which appears when the outer layer of lead oxide that is constantly becoming thinner finally bursts and the bright noble metal shines through. Just before the blick there is a distinct iridescence, so that the point can never be mistaken. At once remove from the muffle and, after cooling, observe the color of the button.

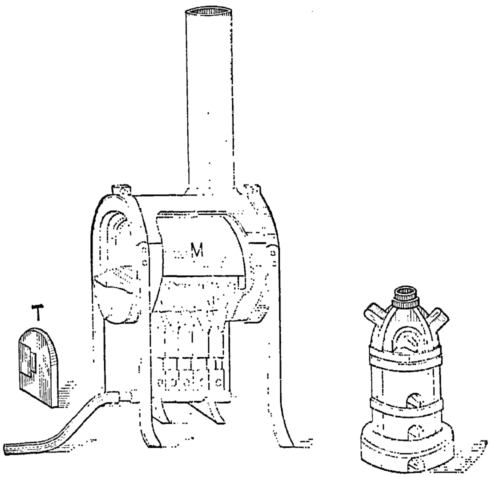

Fig. 58.

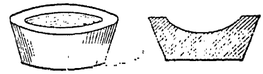

Fig. 59.

(*a*) *If the button is greenish yellow or darker*, it contains less than three parts of silver to one part of gold, in which case add from 4 to 6 parts of "fine silver" (the proper amount can be usually told by the practiced eye) and heat again in a new cupel with 1 g of lead. Treat the button now obtained with nitric acid and weigh the residual gold.

(*b*) *If the button is pure white*, then three or more parts of silver are present to one part of gold. In this case it is immediately "parted" and the residual gold weighed.

After the approximate amount of gold present has been ascertained,* the analysis proper is made, using the amount of lead as indicated in the following table:

* In assay laboratories the approximate gold contents of the alloy is determined by its streak. A fine-grained piece of silicate is blackened with charcoal. The alloy to be tested is rubbed upon it and the color produced compared with that obtained from alloys containing known amounts of gold. Afterwards these streaks are tested with dilute aqua regia; alloys containing the same amounts of gold are attacked equally readily.

LEAD TABLE

Approximate Percentage of Gold in the Alloy	Amount of Lead Necessary for the Cupellation of 0.25 g of Alloy
100 per cent	0.25 g
90 "	2.50 "
80 "	4.00 "
70 "	5.50 "
60 "	6.00 "
50 "	6.50 "
40 or less "	8.50 "

The Final Assay

For the definite determination of the gold and silver, take two portions weighing exactly 0.25 g, the one to serve for the silver determination and the other for the gold. Cupel the former with the correct amount of lead and determine the weight of the gold-silver button.

If the original alloy was very white, it contains more than 50 per cent (500 thousandths fine) of silver.

If the alloy was greenish yellow, it probably contains 55–75 per cent of noble metal, and silver is present to a considerable extent. If, however, the alloy was a beautiful yellow or reddish yellow, it contains more than 70 per cent of gold.

For a white alloy, therefore, weigh out a quantity of pure silver equal to the weight of gold as indicated by the preliminary assay (inquartated with one part of silver), and cupel this mixture with the same amount of lead as the first portion.

In the case of a greenish yellow alloy, inquartate* with two parts of silver; and for a distinctly yellow or reddish yellow alloy, inquartate with $2\frac{1}{2}$ parts of silver.

Treatment of the Quartered Gold-Silver Button

Remove the gold-silver button from the cupel with the "button tongs," clean with a stiff brush ("button brush"), and hammer upon an anvil to a round disk about 1 mm thick (Fig. 60, *a*). Heat this upon a fresh cupel and quickly cool by placing it upon a piece of brass foil and rolling it between two steel rollers to a long strip (Fig. 60, *b*); again heat and roll† up as shown in Fig. 60, *c*. Place this little roll in a small flask (Fig. 61, I), cover with 30–40 ml of nitric acid (*d.* 1.188)

* Cf. p. 252.

† By hammering the gold-silver alloy, the metal becomes so brittle that it cannot be converted to a smooth-margined roll, and on the subsequent treatment with nitric acid, little pieces would probably drop off. By again heating the metal and then quickly cooling, it regains its original softness.

free from chloride, heat to boiling and keep boiling gently for 10 minutes. Pour off the acid, replace by the same quantity of stronger acid (*d.* 1.295), and repeat the above treatment. After this pour off acid and wash the button, decanting three times with distilled water. Fill the flask with water, cover with an annealing cup (or, lacking this, an ordinary porcelain crucible may be used), and quickly invert (Fig. 61, II); the gold will pass into the cup. Remove the flask by first raising

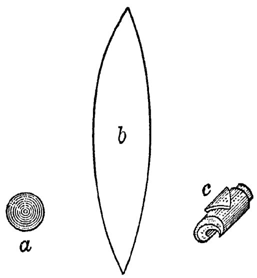

FIG. 60.

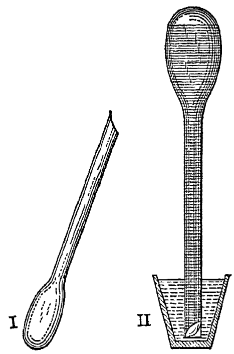

FIG. 61.

its mouth to the level of the water in the crucible and then slide it off at right angles and skilfully turn the flask right side up. Pour off the water from the gold and place the crucible in the back part of the muffle for a short time, whereby the gold is dried and is changed from its former brown and soft condition into a harder, beautiful yellow substance. Cool and weigh. By subtracting the weight of the gold from the weight of the gold and silver together, the amount of silver is determined.

Determination of Gold in Ores

Principle. — The very finely ground and sifted ore is mixed in a No. 9 French crucible with lead oxide, charcoal, and some suitable slag-forming material. The charcoal reduces a part of the lead oxide to metal which alloys with the noble metal and sinks to the bottom in the form of a button, while the foreign substances pass into the slag. After cooling, break the crucible, hammer off the slag, cupel the lead button, and part the silver-gold button in the usual way. The noble metal should be extracted with as little lead as possible, for with an unnecessarily large amount of lead some gold is lost during the cupellation.

The amount of lead reduced from the litharge depends largely upon the nature of the ore. Sulfide ores act strongly reducing, as is shown by the following equations:

$$S + 2\,PbO = SO_2 + 3\,Pb$$

$$FeS_2 + 5\,PbO = 2\,SO_2 + FeO + 5\,Pb$$

In such cases less charcoal (or in some cases none at all) should be added than would be otherwise necessary to produce the right amount of lead. Sometimes, when considerable sulfide is present, it is necessary to neutralize its action by the addition of oxidizing agents.

Reducing ores are recognized by their color: they are gray, bluish black, or yellow (pyrite, etc.). Reddish brown ores (Fe_2O_3) usually act oxidizing:

$$Fe_2O_3 + C = CO + 2\,FeO$$

in which case more charcoal must be added to the charge.

The best results are obtained if the lead button weighs about 18 g when obtained from 30 g of ore.* In order that such a button may be obtained, it is usually necessary to make a preliminary assay of the ore. But above all, it is necessary that the purity of the reagents used should be tested.

Testing the Reagents

The ordinary reagents necessary for a gold assay are:

1. Litharge (PbO)

Litharge, the most important reagent, is a basic flux, for it forms with the silicic acid of the ore a readily fusible silicate. At the same time, it is a desulfurizing agent, as is shown by the above reaction.

The litharge used must be dry and free from minium, for the latter oxidizes silver, carrying it into the slag, so that low results would be obtained in the silver determination. The litharge should be free from silver (which is almost never the case), or its silver contents must be known; this is determined once for all by the following experiment: Mix 120 g of litharge, 60 g of sodium bicarbonate, and 2 g of argols (crude $KHC_4H_4O_6$) upon a sheet of glazed paper; place the mixture in a No. 9 French crucible and cover with a layer of finely powdered, dry common salt. Place the covered crucible in a hot coke-oven.

As soon as the contents of the crucible have reached the state of quiet fusion, remove the crucible from the fire, gently tap its walls with the tongs, and tap lightly upon its bottom to knock down any small particles of lead adhering to the sides and to make all the free metal collect together on the bottom in the form of a button.

After cooling break the crucible, remove the slag from the lead button by hammering it upon an anvil, and subject it to cupellation, using a cupel weighing only a few grams more than the button itself. Weigh the resulting silver button, and deduct this weight of silver whenever the corresponding amount of litharge is used in an assay.

* This amount is usually sufficient; with very rich gold ores 10–15 g is enough, whereas with very poor ores as much as 120 g may be used to advantage.

2. Sodium Bicarbonate ($NaHCO_3$)

3. Anhydrous Borax ($Na_2B_4O_7$)

2 and 3 require no testing.

4. Charcoal

The reducing power is determined as follows: Mix 60 g of litharge, 15 g of sodium bicarbonate, and 1 g of charcoal, as in the testing of litharge, in a French crucible No. 9, cover with common salt, and fuse. After cooling, determine the weight of the lead button; this expresses in terms of lead the reducing power of the charcoal.

One gram of charcoal should reduce about 30 g lead.

5. Niter (KNO_3)

serves as an oxidizing agent. Its oxidizing power expressed in terms of lead is determined: Mix 3 g of niter (potassium nitrate), 60 g of litharge, 1 g of charcoal, and 15 g of sodium bicarbonate, fuse as before, and determine the weight of the lead button. If under (4) it was found that 1 g of charcoal would reduce P grams of lead, and if p grams of lead were obtained in this experiment, then the difference $P - p$ shows the amount of lead that was oxidized by 3 g of niter, or the oxidizing power of the niter.

One gram niter oxidizes about 4 g lead.

6. Common Salt

Heat table salt in a large Hessian crucible until it melts, and pour the contents of the crucible into a shallow iron mold with a raised edge. Powder and preserve in a stoppered flask.

After the reagents have all been tested the next step is the

Preliminary Assay

Weigh out 5 g of the finely powdered and sifted ore and mix with 80 g of litharge, 20 g of sodium bicarbonate, and 5 g of borax. Place the mixture in a crucible and cover with a layer of common salt. After fusing, cooling, and hammering off the slag, as already described, weigh the lead button.

Since in an ordinary assay about 30 g of ore are taken, the weight of the lead button now obtained multiplied by 6 will give the weight of the button from the real assay. Four cases will be considered.

(1) *The lead button weighs* 3 *g*

A button obtained from 30 g of ore would weigh 18 g. In this case, assay the ore with the following proportions of flux: 80 g of litharge, 20 g of sodium bicarbonate, and 5 g of borax.

(2) *The lead button weighs less than* 3 *g*

Evidently the ore has a slight reducing action, but not enough to yield a button weighing 18 g when 30 g of ore are used; it is, therefore, necessary to add charcoal to the **flux**.

Example. — Assume that the lead button obtained by the preliminary assay weighed 1 g, then the button obtained from 30 g of ore would weigh 6 g. In order to obtain a button weighing 18 g it is necessary to add enough charcoal to supply 12 g of lead. If 1 g of charcoal was found to reduce 30 g of lead, then it is necessary to add 12 ÷ 30 g = 0.4 g of charcoal.

(3) *The lead button weighs more than* 3 *g*

In this case the ore has a strong reducing power, and to obtain the lead button of the right weight it is necessary to add some niter.

Example. — Suppose the button to weigh 6 g; this would mean a 36-g button when 30 g of ore were used; *i.e.*, 18 g too much lead would be produced. We must add, therefore, enough niter to oxidize this 18 g of lead. If the oxidizing power of 1 g of niter was found to be 4 g of lead, then 18 ÷ 4 = 4.5 g of niter must be added to the flux.

Remark. — Ores which have a very strong reducing power would frequently require the addition of enough niter to cause the contents of the crucible to boil over. In such a case, place 40–50 g in a "roasting-dish," roast in a muffle, and from this roasted ore take portions for the preliminary and final assays. The results, however, must be expressed in terms of the unroasted ore.

(4) *No lead button is formed*

The ore is either neutral or possesses an oxidizing action. Repeat the assay using 1 g of charcoal, and base the final assay from the results now obtained.

Final Assay

For convenience, it is customary to weigh out the ore in *assay ton* units. Ore is usually weighed in avoirdupois tons and gold in troy ounces. The assay report usually gives the ounces troy contained in a ton avoirdupois. Since there are 29,166 troy ounces in an avoirdupois ton, the assay ton is made equal to 29.166 g. Then if one assay ton of ore is used each milligram of gold obtained will represent *one ounce per ton.* For weighing out the ore an inexpensive balance (pulp balance) can be used. It should be capable of taking a load of 200 g but need not be sensitive to less than 1 mg. For weighing the gold or silver buttons, a *button balance* sensitive to 0.01 mg should be used.

For the final assay use from 0.1 to 5 assay tons of ore (according to the amount of gold present) and the corresponding amount of the vari-

ous fluxes. Otherwise the procedure is exactly the same as in the preliminary assay. Cupel the lead button and part the weighed silver-gold button as described on p. 254.

Platinum, Pt. At. Wt. 195.2

Platinum is best determined as metallic platinum. The following three cases will be considered:

1. The platinum is present in a hydrochloric acid solution either alone or together with other metals, but other platinum metals are absent.
2. The platinum is present alloyed with gold and silver.
3. The platinum is alloyed with small amounts of the platinum metals together with small amounts of base metals.

1. The Platinum is Present in Hydrochloric Acid Solution Either Alone or Together with Other Metals

The platinum is either precipitated from the solution as ammonium chloroplatinate, $(NH_4)_2PtCl_6$, which is decomposed by ignition and the residual platinum weighed; or the platinum is precipitated as metal by the addition of reducing agents to the solution; or finally the platinum is precipitated as sulfide by conducting hydrogen sulfide into the hot solution and changed to platinum by ignition. The two former methods serve to separate platinum from most other metals; the latter serves to separate platinum only from the metals of the alkali, alkaline earth, and ammonium sulfide groups, and not from members of the hydrogen sulfide group.

(a) *Precipitation of Platinum as Ammonium Chloroplatinate*

Reduce the volume of the solution as much as possible by evaporation, nearly neutralize with ammonia, add an excess of ammonium chloride and considerable alcohol. Allow the mixture to stand 12 hours under a glass bell-jar. Filter through an asbestos filter tube 10–15 cm long and wash with 80 per cent alcohol until a few drops of the filtrate leave no residue on being evaporated to dryness on a platinum foil. Dry the precipitate by conducting a stream of air, warmed to about 90°, through the tube. After cooling weigh the tube, introduce a plug of ignited asbestos* and again weigh; thus the weight of the asbestos plug is found. Conduct a stream of dry hydrogen through the tube, and

* Ammonium chloroplatinate decrepitates during the heating. To prevent loss of substance heat it between two asbestos plugs.

heat the tube carefully until no more hydrochloric acid is evolved and all the ammonium chloride has been driven off; then cool the tube in a desiccator and weigh.

Instead of filtering the precipitate upon asbestos, an unweighed paper-filter may be used. Place the moist precipitate together with the filter in a large porcelain crucible so that the apex of the filter paper points upward, and heat very carefully, as otherwise there can be a considerable loss by spattering. At first dry the precipitate by gently heating the partly covered and inclined crucible with a tiny flame under the cover until the odor of alcohol has disappeared. Take care not to burn the alcohol. When all the alcohol has evaporated, slowly raise the temperature until the crucible is at a strong red heat. During the whole operation there must be no visible escape of vapors from the crucible. The decomposition is complete when there is no longer a penetrating odor arising from the crucible. Now place the crucible in an upright position and ignite with free access of air until the carbon from the filter paper is completely burned. Often a slight deposit of platinum* will be found in the upper part of the crucible and upon the cover, so that the cover must always be weighed with the crucible.

Remark. — If it seems likely that the precipitate of ammonium chloroplatinate is contaminated with other substances (*e.g.*, sodium chloride, etc.) the precipitate can be dissolved in water after it has been washed with alcohol and dried. The platinum may then be determined by heating with a little mercury, washing the precipitated platinum with dilute hydrochloric acid and then with water, and finally weighing.

The results obtained by this method are satisfactory but somewhat lower than the true values; the following process is more accurate:

(*b*) *Precipitation of Platinum by Reducing Agents*

Free the solution from any excess of acid by evaporation and transfer to an Erlenmeyer flask the neck of which is ground to fit a return-flow condenser. Neutralize the solution with ammonia, add an excess of formic acid and a little ammonium acetate, dilute to 200 ml, and heat to about 80° C on the water-bath until the evolution of carbon dioxide has nearly ceased. Now connect the flask with the return-flow condenser, and boil for 24 hours. Filter off the precipitated metal, wash with dilute hydrochloric acid then with water, dry, ignite, and weigh.

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* By means of the dry distillation of the filter, carbon monoxide is formed; and by the decomposition of the ammonium chloroplatinate, chlorine is set free. These two gases act upon the metallic platinum and form volatile compounds ($PtCl_2 \cdot CO$, $PtCl_2 \cdot 2CO$, and $2PtCl_2 \cdot 3CO$), which, however, are later decomposed by the aqueous vapor. This causes the deposit of platinum in the upper part of the crucible. In order to avoid loss, à large crucible should be used.

2. Determination of Platinum in Alloys

Platinum is now used a great deal in jewelry and there are so many useful alloys of platinum that the analysis has become of importance. The platinum content is almost always determined by dry assay.

Weigh out 0.1 g of the alloy and make a trial assay to determine the approximate platinum content. Cupel twice with 1-g portions of lead at a high temperature (well back in the hot muffle), weigh the resulting button, and part with sulfuric acid as described below. For the analysis proper, weigh out 0.25 g of alloy; add 1.25 g of pure silver and the same quantity of copper. Cupel at a white heat, using 15 g of lead if the alloy is nearly pure platinum and reducing the quantity of lead by 0.15 g for each per cent of alloyed metal but using at least 2 g.

After the cupellation place the button on a fresh cupel and heat 2–5 minutes in the hottest part of the muffle. Hammer out the button and roll it until it is 0.2 mm thick. Part the button in a small Jena flask, using 20–30 ml of concentrated sulfuric acid which has been diluted with 22 per cent of water by volume. Heat the metal with the sulfuric acid for 15 minutes at 240°. Nitric acid could not be used for the parting as it dissolves some platinum as well as silver. By boiling platinum with pure concentrated sulfuric acid, 7.7 mg are dissolved in an hour but dilution prevents the dissolving. By keeping the temperature at 240° there is no appreciable loss of platinum.

After the heating allow the acid to cool, carefully decant off the liquid, and repeat the acid treatment twice more. To avoid loss by bumping during the second and third treatments, wind a piece of pumice with platinum wire and drop it into the flask. After the third treatment, decant off the acid and wash the residual platinum twice by decantation with water. During the decantation some platinum always flows off with the liquid. Save the washings, therefore, filter through a small filter, ignite, and weigh in a crucible. Transfer the most of the platinum to a porcelain crucible, rinse off the pumice, and evaporate off the water. Ignite and weigh.

Separation of Platinum from Gold

Parting with sulfuric acid leaves gold, if present, with the platinum. Parting with nitric acid does not dissolve platinum in the absence of silver but, if three parts by weight of silver are present for each part of gold and platinum, the platinum gradually dissolves.

Procedure. — Cupel the platinum-gold button, obtained by the above method of assaying, with three times its weight of pure silver and 1 g of lead. Hammer and roll the resulting button and part with

$6\,N$ nitric acid. Weigh the button, inquartate with 3 parts of silver, and again cupel with 1 g of lead. This time part with $9.5\,N$ nitric acid. Repeat the inquartation and parting until a constant weight of gold is obtained.

Instead of separating gold and platinum in this way, the button can be dissolved in aqua regia and the gold precipitated by ferrous sulfate as described on p. 250 or the gold may be thrown down from an alkaline solution by means of hydrogen peroxide. It may be necessary to dissolve the gold in aqua regia and repeat the precipitation. To determine the platinum, precipitate it as sulfide by introducing hydrogen sulfide into the hot acid filtrate and weigh as metal after ignition in a porcelain crucible.

3. Analysis of Commercial Platinum, according to Deville and Stas

Heat 5 g of the platinum alloy for 5 hours at about 1000° with ten times as much lead in a crucible of purified gas-carbon embedded in a clay crucible filled with charcoal. After cooling, treat the lead button with very dilute nitric acid until gas is no longer evolved.

In this way a **solution, A,** is obtained, containing about 98.4 per cent of the lead used, all the palladium and copper, and small amounts of platinum, rhodium, and iron, and a **residue, B,** consisting of a black metallic powder, which is filtered off, and will contain the remainder of the platinum and rhodium with all the iridium and ruthenium.

1. *Treatment of the Nitric Acid Solution A*

Precipitate the lead by adding a slight excess of sulfuric acid, and filter. If the lead sulfate is pure white, wash it with $2\,N$ sulfuric acid. If it is not absolutely white, wash it with a solution of ammonium carbonate until it becomes so; small amounts of lead are dissolved by this operation. Concentrate this last wash liquid, therefore, to precipitate lead carbonate, filter, and after making acid with hydrochloric acid, add the solution to the main filtrate.

Evaporate to about 100 ml, and when cold pour into a saturated solution of ammonium chloride. Heat to boiling and allow to cool again. Filter off the ammonium chloroplatinate and wash with a saturated solution of ammonium chloride; in this way, the greater part of the platinum is obtained.

Boil the filtrate from the platinum precipitate with formic acid and ammonium acetate as described on p. 260, *b*. In this way the remainder of the platinum, the palladium, and the rhodium will be precipitated. Filter off these metals, and determine the copper and iron in the filtrate

by the usual method. Dry the formic acid precipitate (consisting of a black metallic powder) and fuse with potassium pyrosulfate in a porcelain crucible. Treat the melt with water, decant the solution from the unattacked platinum, and wash alternately with ammonium carbonate and nitric acid (to remove traces of lead sulfate), then with dilute hydrofluoric acid, and finally with water. Dry and weigh the platinum. The filtrate from the platinum contains palladium and rhodium. Precipitate the former by adding mercuric cyanide, and boiling until the odor of hydrocyanic acid has disappeared. Wash the voluminous yellowish white precipitate of palladous cyanide first by decantation and then upon the filter. Dry, and ignite at first cautiously and then strongly over the blast until the paracyanide is completely destroyed; finally heat in a current of hydrogen (as in the case of copper sulfide, p. 193) to reduce any palladium that has been oxidized by the previous treatment. As soon as the flame is removed, at once cut off the supply of hydrogen to prevent its being absorbed by the metal. Weigh the cold palladium.

Precipitate the rhodium from the filtrate by means of formic acid, as before, dry the deposited metal, ignite in a stream of hydrogen, allow to cool in the gas, and weigh.

2. *Treatment of the Residue B*

Heat the washed residue with dilute aqua regia (2 vols. nitric acid, 8 vols. hydrochloric acid, and 90 vols. water), and in this way **solution C** is obtained, which contains the rest of the lead, platinum, and rhodium, and **residue D**, consisting of lamellæ of iridium and ruthenium.

3. *Treatment of the Solution C*

After evaporating to a small volume, remove the lead by sulfuric acid. Evaporate the filtrate from the lead sulfate to dryness, take up the residue in hydrochloric acid, and precipitate the platinum by pouring into a cold saturated solution of ammonium chloride, continuing as described under 1, p. 259. The platinum precipitate contains a little rhodium.

Wash the precipitate with half-saturated ammonium chloride solution and then twice with a little cold water. Set the filtrate aside.

Rinse back the precipitate into the precipitating-vessel, and wash the filter thoroughly with boiling-hot water. Make the volume of liquid about 150 ml for each gram of Pt. Add a little HCl, heat to boiling, and pass a brisk stream of chlorine through the liquid until the precipitate dissolves, forming H_2PtCl_6 again. Add 6 ml of 10 per cent NH_4Cl

solution for each gram of Pt, evaporate to about 20 ml, and dilute with an equal volume of half-saturated NH_4Cl solution. After a few hours filter off the pure precipitate of $(NH_4)_2PtCl_6$. Ignite and weigh as usual (see p. 259).*

The combined filtrates from the platinum contain rhodium and still a little platinum. Add once more ammonia, acetic and formic acids, and boil the solution for a long time. Filter off the precipitated metal, ignite and weigh. Fuse this precipitate at a red heat with potassium pyrosulfate, and extract the cold melt with water. If a residue remains after this treatment, filter off, weigh, and treat with dilute aqua regia. If it dissolves, it is platinum; if it does not, it is rhodium.

Dilute the filtrate from the ammonium chloroplatinate, which contained some rhodium, add formic acid and ammonium acetate, and gently boil for 2 or 3 days in an Erlenmeyer flask connected with a return-flow condenser. The liquid evaporates somewhat in spite of the condenser, and it is necessary to replace the evaporated part from time to time with a dilute solution of ammonium formate. In this way small amounts of platinum and rhodium are precipitated. Filter them off and separate by fusion with potassium bisulfate as before. In the filtrate traces of platinum, rhodium, and iron are likely to be present.

First remove the iron by the addition of chlorine water and afterward ammonia; filter off the ferric hydroxide, ignite, and weigh. To remove the last traces of platinum and rhodium, evaporate this last filtrate to dryness, heat the residue with nitric acid to remove the ammonium chloride completely, and then boil for a long time with formic acid and ammonium acetate. Wash the traces of metal thus obtained with hydrofluoric acid and add to the main portion of platinum and rhodium.

4. *Treatment of the Residue D*

Filter off the undissolved, gray lamellæ (consisting of iridium, ruthenium, and small amounts of iron) obtained after the above treatment with dilute aqua regia. Dry, ignite in an atmosphere of hydrogen or illuminating gas, and weigh.

Fuse the weighed metal in a pure gold crucible with potassium nitrate and carbonate. For this purpose, place a previously melted mixture of 3 g potassium nitrate and 10 g potassium carbonate in the crucible, add the metal, and heat the mixture for 2 hours at a dull-red temperature. In this way the ruthenium is changed completely into water-soluble potassium ruthenate, K_2RuO_4, and the iridium is

* Schoeller, *Analyst*, **55**, 550 (1930).

oxidized to Ir_2O_3; the latter forms, to some extent, a soluble compound with the alkali.

Extract the melt with water, and pour the solution, together with the suspended Ir_2O_3,* into a stoppered cylinder, allow the precipitate to settle, and decant off the clear liquid into a retort.

Repeatedly cover the residue remaining in the cylinder with a dilute solution of sodium hypochlorite and sodium carbonate, until the yellow color is completely removed. Add the decanted liquid to the main solution in the retort. This solution contains all the ruthenium and a part of the iridium. Saturate with chlorine in the cold, distil and receive the distillate in a mixture of alcohol (distilled over potassium) and pure hydrochloric acid.

After the distillation is complete, evaporate the alcoholic distillate to dryness and reduce the ruthenium chloride thus obtained to metal by heating in a stream of hydrogen. After weighing, test the purity of the ruthenium. It should dissolve completely in a concentrated solution of sodium hypochlorite.

Evaporate the liquid remaining in the retort to a small volume, add the insoluble residue that remained in the cylinder after the above treatment with sodium hypochlorite solution, and boil the mixture with caustic soda solution, with the addition of a little alcohol, until all the iridium is precipitated.

Filter off the dark blue precipitate, consisting of iridium oxide and small amounts of ferric hydroxide, wash, and strongly ignite. Dissolve out the contaminating ferric oxide by heating with hydrochloric acid containing some ammonium iodide, and wash the residual iridium oxide successively with water, chlorine water, and hydrofluoric acid, to remove gold that came from the crucible and silicic acid from the caustic soda. Ignite in hydrogen and weigh the iridium.

Precipitate the iron in the hydrochloric acid extract as ferric hydroxide, ignite, and weigh. Test its purity by heating in a stream of hydrogen and hydrochloric acid, to see if it can be completely changed to ferrous chloride and volatilized as such.

F. Mylius and F. Förster† have recommended that platinum be tested for small amounts of impurity by taking three separate portions each weighing 10 g. Test the first portion for palladium, iridium, and ruthenium according to the lead procedure just described of Deville and Stas. The second portion serves for the iron determination; dissolve the metal in aqua regia, precipitate the platinum metals by formic

* Cf. W. Palmaer, *Z. anorg. Chem.*, **10**, 332 (1896).

† *Ber.* **1892**, p. 665.

acid, and determine the iron in the filtrate. In the third portion determine rhodium, silver, copper, and lead by volatilizing the platinum as $PtCl_2CO$ at 238° (temperature of boiling quinoline) in a stream of carbon monoxide and chlorine, and determining the other metals in the residue.

Remark. — The determination of the iron in a separate portion is to be recommended, for in the lead procedure some iron is always obtained from the carbon crucible.

PALLADIUM, Pd. At. Wt. 106.7

In the older methods of analysis, palladium was usually determined as metal. Although some palladic salt is formed when the metal is dissolved in aqua regia, bivalent palladous chloride, $PdCl_2$, is formed on evaporating with concentrated hydrochloric acid. From a slightly acid solution of palladous chloride, the free metal can be deposited easily by heating with sodium formate solution or by passing carbon monoxide into the cold, slightly acid solution. The deposited metal can be filtered off, ignited, and weighed. Palladium also forms some insoluble salts that can be used for quantitative analysis. Thus palladous cyanide, $Pd(CN)_2$, palladous iodide, PdI_2, and palladous nitrosonaphthol, $Pd(C_{10}H_6NO_2)_2$, have been recommended for determining palladium. In the first two cases, the similarity of palladous salts to silver salts will be noticed, and in qualitative analysis palladium is precipitated in the first group. In the case of the nitrosonaphthol compound, the analogy to cobalt will be noticed. This is not surprising, for palladium, like cobalt, belongs in the eighth group of the periodic table of the elements. To-day, the most characteristic reagent for palladium is dimethylglyoxime which is used so much for determining nickel, another eighth-group element. By means of this reagent, it is possible to separate palladium from the other platinum metals; and the precipitate can be weighed. Gold must absent or it will precipitate as metal. The only objection that can be raised to dimethylglyoxime as a reagent for palladium is the fact that the precipitate is very voluminous and when much of it is present it may be difficult to handle. In such cases precipitation of the cyanide or of the iodide may be used. Both $Pd(CN)_2$ and PdI_2 are sufficiently insoluble to provide satisfactory separations. The iodide is soluble in an excess of potassium iodide solution so that care must be taken to use only a slight excess of reagent, and rhodium iodide, RhI_3, may precipitate if much rhodium is present. Potassium iodide also gives a deep red color with H_2PtCl_6 on account of the formation of H_2PtI_6; this reaction has been recommended for detecting platinum.

(*a*) Determination with Dimethylglyoxime

Procedure. — To the moderately acid solution (it can be $0.25\,N$ in HCl or HNO_3) containing not more than 0.1 g of Pd in 250 ml add at room temperature a 1 per cent solution of dimethylglyoxime in 95 per cent alcohol. For each milligram of palladium present, use about 0.25 ml of the reagent (0.0025 g of solid). Allow the solution to stand for half an hour at about 40° or for an hour at room temperature and then filter through a weighed Gooch crucible. To the filtrate add a little

more of the reagent to make sure that the precipitation is complete. Wash the orange-yellow precipitate of $Pd(C_4H_7N_2O_2)_2$ thoroughly, first with cold and then with hot water, dry at 110°, and weigh. The precipitate contains 31.67 per cent of palladium.

If it is desired to repeat the precipitation, as is sometimes necessary when much platinum is present, filter through a paper filter and digest the precipitate with 25 ml of aqua regia which has been diluted with an equal volume of water. Dilute, filter, burn the filter, digest the ash with aqua regia, dilute, and filter into the main solution.

If more than 0.1 g of palladium is present, it is well to work with an aliquot part of the solution, or an ashless filter paper can be used for filtering off the bulky precipitate. Transfer to a weighed porcelain crucible, dry, ignite slowly, and cool in a stream of hydrogen. Finally uncover the crucible and heat momentarily to redness to drive off most of the occluded hydrogen from the palladium metal. (If a metallic sublimate forms on the sides of the crucible, the ignition has not been properly done.) Moisten the residue with 2 or 3 drops of formic acid, and heat the crucible and its contents on a hot plate to evaporate off the excess formic acid, and finally weigh as Pd.

(*b*) Precipitation of Palladium by Formic Acid

To the fairly dilute solution add sodium formate solution, cover with a watch glass, and heat carefully over a free flame. Carbon dioxide is evolved and shortly the palladium is precipitated as a fine black powder: $PdCl_2 + HCO_2Na = NaCl + HCl + CO_2 + \mathbf{Pd}$. The finely divided metal is appreciably soluble in hydrochloric acid. After the evolution of gas has ceased, therefore, add sodium carbonate solution until a neutral or faintly alkaline reaction is obtained. Filter and wash the palladium with hot water. Place the moist filter and precipitate in a porcelain crucible and carefully ignite, finally using the full heat of the burner. Cool and weigh. As a rule, there is a slight superficial oxidation of the metal as shown by blue or violet colorations, but the increase in weight is so small that it can be neglected.

(*c*) Precipitation of Palladium as Palladous Cyanide

Nearly neutralize the solution with sodium carbonate and add an excess of mercuric cyanide: $PdCl_2 + Hg(CN)_2 = HgCl_2 + \mathbf{Pd(CN)_2}$. Heat on the water-bath until there is no more odor of hydrocyanic acid, allow the light yellow precipitate to settle, wash it by decantation and on the filter with cold water. Dry, ignite, and weigh as Pd.

Separation of Palladium from Platinum

Evaporate the hydrochloric acid solution to dryness. If any nitric acid was present, add more hydrochloric acid and again evaporate to

dryness, because it is necessary for the success of this separation that all the palladium shall be in the bivalent condition. Otherwise, insoluble $(NH_4)_2PdCl_6$ will be formed together with the corresponding platinum compound.

To the residue add a slight excess of solid ammonium chloride. Moisten with a little water, and after a short time add some saturated ammonium chloride solution (38 per cent). Stir well, allow to stand for some hours, then filter off the $(NH_4)_2PtCl_6$ precipitate. Wash with strong ammonium chloride solution and treat the precipitate as described on p. 259.

In the filtrate determine the palladium as the palladous salt of dimethylglyoxime.

SELENIUM, Se. At. Wt. 78.96

Selenium is usually determined as the element itself. Two cases are to be considered:

I. The selenium is present as alkali selenite or as selenious acid.
II. The selenium is present as alkali selenate or as selenic acid.

I. *The selenium is present as selenite or as free selenious acid.* — Make the solution acid with hydrochloric acid, saturate with sulfur dioxide gas, boil, filter through a Gooch crucible, and wash first with water then with alcohol. Dry the residue at 105° and weigh.

Remark. — The precipitation of selenium by sulfur dioxide is quantitative whether the solution is concentrated or dilute, but it takes place more readily in the presence of considerable acid. This fact is of importance in the separation of selenium from tellurium, for the latter element is not precipitated by sulfur dioxide when considerable hydrochloric acid is present (cf. p. 270).

In the presence of nitric acid the precipitation of selenium by sulfurous acid is incomplete. In such cases, the nitric acid may be removed by boiling with hydrochloric acid in a flask under a return-flow condenser. Evaporation in an open vessel is not permissible as considerable selenium is volatilized even in the presence of dissolved alkali chloride. It is safer to precipitate the selenium with hydrazine sulfate or hydrazine hydrate when nitric acid is present.

Add ammonium hydroxide to the nitric acid solution until it is faintly ammoniacal and then make slightly acid with hydrochloric acid. Cover the Erlenmeyer flask with a watch glass, add an excess of hydrazine sulfate or hydrate, and boil until the precipitated red selenium coagulates and changes into the easily filtrable gray modification with a clear supernatant solution. Filter into a Gooch or Munroe crucible, wash

with hot water and then with alcohol, dry at 105°, and weigh the selenium.

Phosphorous acid does not precipitate selenium from cold, dilute, strongly acid solutions; this fact is made use of in the separation of selenium from mercury (cf. p. 272).

II. *The selenium is present as alkali selenate or as free selenic acid.* — As selenium in the form of selenic acid is not precipitated by sulfur dioxide, phosphorous acid, or hydrogen sulfide, it must be first reduced to selenious acid by long-continued boiling with hydrochloric acid (cf. Vol. 1); the above procedure is then followed. This tedious operation is unnecessary, however, if the precipitation is effected with hydrazine hydrate or sulfate as described under I.

In practice, selenium is obtained usually in neither of the above forms, but as impure selenium (selenium sponge) or as selenide, and by the treatment of these substances one or the other of the above selenium compounds is obtained.

If the selenium or selenide is made to react with concentrated nitric acid,* or aqua regia, all of it is dissolved in the form of selenious acid (not selenic acid), and the selenium can be precipitated with hydrazine hydrate or sulfate as described under I.

If the finely powdered selenium or selenide is intimately mixed with two parts sodium carbonate and one part potassium nitrate, placed in a nickel crucible, covered with a layer of sodium carbonate and potassium nitrate, and heated gradually until it fuses, all the selenium forms alkali selenate and on extracting the melt with water it goes into solution; in this way it is separated from most of the remaining oxides. The solution, however, often contains small amounts of lead. In order to remove lead, treat the filtrate with hydrogen sulfide, and again filter; free the solution from hydrogen sulfide by boiling, strongly acidify with hydrochloric acid, boil until no more chlorine is evolved, and precipitate the selenium by sulfur dioxide according to II.

Remark. — The mixture must be heated very slowly, as otherwise some selenium is likely to be lost by volatilization.

TELLURIUM, Te. At. Wt. 127.6

Tellurium is usually determined as the element itself.

If sulfur dioxide is conducted into a hydrochloric acid solution containing tellurous acid, black tellurium is precipitated quantitatively, *provided the solution does not contain too much acid.* If tellurous acid is dissolved in 200 ml of concentrated hydrochloric acid, no tellurium will

* Mercury selenide is unacted upon by nitric acid, but is dissolved by aqua regia.

be precipitated on passing sulfur dioxide into the cold solution. If, however, the solution is diluted with an equal volume of water and sulfur dioxide is passed into the boiling solution, all the tellurium will be precipitated. Filter off the precipitate, wash with water until free from chlorides, then with alcohol, dry at 105°, and weigh. The oxidation of the tellurium during the drying is so slight that it can be disregarded.

From solutions of telluric acid, tellurium is not precipitated by means of sulfur dioxide. From such solutions the precipitation can be accomplished by boiling for a long time under a return-flow condenser with strong hydrochloric acid which reduces telluric acid. According to Gutbier, this reduction is unnecessary if hydrazine hydrochloride or hydrate is used to precipitate the tellurium.

$$2\,H_6TeO_6 + 3\,(N_2H_4 \cdot 2HCl) = 12\,H_2O + 6\,HCl + 3\,N_2 + 2\,Te$$

Lenher and Homberger prefer to use both hydrazine hydrochloride and sulfurous acid. Their procedure is as follows: To the solution of tellurite, tellurate, or the corresponding acids, containing about 0.5 g of tellurium, add 25 ml of 3 N hydrochloric acid, 10 ml of a 15 per cent solution of hydrazine hydrochloride, and 35 ml of saturated sulfur dioxide solution. Boil 5 minutes, filter, wash with hot water till free from chloride, then with alcohol, dry at 105°, and weigh as tellurium. The entire analysis can be made in an hour.

Separation of Selenium and Tellurium from the Metals of Groups III, IV, and V

By conducting sulfur dioxide into the solution fairly acid with hydrochloric acid, the selenium and tellurium will be quantitatively precipitated while the other metals remain in solution.

Separation of Selenium and Tellurium from the Metals of Group II

(a) *From Copper, Bismuth, and Cadmium*

Pass sulfur dioxide into the boiling solution, acid with hydrochloric acid, whereby all the selenium and tellurium and usually some of the bismuth are precipitated. Filter and wash the precipitate with hot water. Dissolve it in nitric acid, evaporate the solution to dryness, take up in concentrated hydrochloric acid, dilute with a little water, and precipitate with hydrogen sulfide. Wash the precipitate, consisting of the sulfides of selenium, tellurium, and bismuth, and treat with sodium sulfide solution; selenium and tellurium pass into solution while the bismuth remains behind as its brown sulfide and is filtered off.

Make the solution containing the selenium and tellurium acid with

nitric acid, carefully evaporate to dryness, and boil the residue with 200 ml of concentrated hydrochloric acid, until there is no longer any evolution of chlorine. Filter off the deposited sulfur through a Gooch crucible, and saturate the filtrate with sulfur dioxide gas; all the selenium is in this way precipitated. Filter off the selenium through a Gooch crucible and wash successively with 10 *N*, 6 *N*, and 2 *N* hydrochloric acid, and finally with absolute alcohol. Dry the precipitate at 105° and weigh. Dilute the filtrate with an equal volume of water and precipitate the tellurium by passing sulfur dioxide into the boiling solution. Wash this precipitate with water until free from chlorides, then with absolute alcohol, dry at 105°, and weigh.

Remark. — The above method is suitable for the separation of selenium and tellurium from small amounts of bismuth, but does not effect a good separation of selenium (and tellurium) from copper. In this case, more or less copper selenide is formed according to the conditions, and this compound is not decomposed quantitatively by sodium sulfide.* The following method of B. Brauner and B. Kuzma† is more satisfactory.

Precipitate the tellurium and selenium in a pressure-flask, by means of SO_2, filter off the precipitate, which is contaminated with copper, antimony, and bismuth (using a Gooch crucible), wash, dissolve in nitric acid, evaporate the solution to dryness, and take up the residue in caustic potash solution (1 : 5). To the alkaline solution in an Erlenmeyer flask upon a water-bath, add little by little 4–6 g of ammonium persulfate, whereby the potassium tellurite is oxidized to potassium tellurate and the selenite to selenate. When all the persulfate has been added, boil the solution to decompose the excess of persulfate, make acid with sulfuric acid, and allow to cool. Now, add 100 ml of H_2S-water, expel the excess of the H_2S by passing CO_2 through the solution, filter off the precipitated CuS (Bi_2S_3, Sb_2S_3), and treat as described on p. 228. Boil the filtrate with hydrochloric acid to reduce the telluric acid to tellurous acid, reduce the solution by SO_2, and analyze as described above.

The first filtrate from the impure Te and Se will contain the greater part of the Cu, Bi, etc.

(*b*) *From Antimony, Tin, and Arsenic*

If considerable antimony is present, add tartaric acid to the solution, and precipitate the selenium and tellurium by boiling with sulfur dioxide.

According to Muthmann and Schröder‡ this method of separating

* Cf. E. Keller, *J. Am. Chem. Soc.*, **19**, 771.

† Ber., **1907**, 3362.

‡ *Z. anorg. Chem.*, **14**, 433 (1897).

tellurium from antimony is not quantitative; some antimony is always precipitated with the tellurium. A. Gutbier,* however, finds that a perfect separation can be accomplished by means of hydrazine hydrochloride (not the sulfate).

(c) *From Mercury*

Dissolve the mercury selenide, or telluride, in aqua regia, add chlorine water, and dilute the solution largely with water. Add phosphorous acid;† after 24 hours' standing, the mercury is precipitated completely as mercurous chloride, and can be determined as such according to p. 183. Make the filtrate slightly alkaline with potassium hydroxide, evaporate nearly to dryness, dilute, and separate the selenium from the tellurium according to the method of Keller (see below).

(d) *From Gold and Silver*

The separation of selenium and tellurium from silver offers no difficulty, inasmuch as the silver can be precipitated by hydrochloric acid and determined as the chloride.

Precipitate the gold as described on p. 250 by oxalic acid and the selenium and tellurium in the filtrate by means of sulfur dioxide. The three metals may also be precipitated together by sulfur dioxide, weighed, and the selenium and tellurium afterward volatilized by roasting, leaving the gold behind.

Tellurium may be separated from gold by precipitating the gold with ferrous sulfate. In the case of selenium, however, it is also precipitated quantitatively by ferrous sulfate from solutions strongly acid with hydrochloric acid.

Separation of Selenium from Tellurium

Method of E. Keller‡

Keller's method is based upon the fact that tellurous acid is not precipitated from solutions strongly acid with hydrochloric acid while selenium is precipitated quantitatively.

Procedure. — Dissolve the mixture of the two elements, obtained by precipitation with sulfur dioxide, in nitric acid and carefully evaporate to dryness. Treat the dry mass with 200 ml of concentrated hydrochloric acid, boil to remove the nitric acid and saturate with sulfur dioxide.

* *Z. anorg. Chem.*, **32**, 263 (1902).

† Selenious and tellurous acids are not precipitated by phosphorous acid from dilute hydrochloric acid solution, but are precipitated from hot concentrated solutions.

‡ *J. Am. Chem. Soc.*, **19**, 771.

Filter off the precipitated selenium through a Gooch crucible, wash first with a mixture of 90 vols. HCl and 10 vols. water, then with dilute hydrochloric acid, then with water until free from chloride, and finally with absolute alcohol. Dry the selenium at 105° and weigh. Dilute the filtrate with an equal volume of water, heat to boiling, precipitate the tellurium by sulfur dioxide and treat like the selenium.

According to Keller, this method gives satisfactory results, as long as the amount of tellurium present does not exceed 5 g. Even then the separation can be effected by increasing the amount of acid to 450 ml.

Determination of Selenium and Tellurium in Crude Copper

Many copper ores contain selenium and tellurium, and the crude copper obtained from such ores always contains these elements. The amount present may be determined, according to Keller,* as follows: According to the amounts of selenium and tellurium present, take 5–100 g of the copper for analysis. Dissolve the sample in nitric acid, and add an excess of ammonia to precipitate the phosphorus, arsenic, antimony, tin, bismuth, selenium, and tellurium together with the ferric hydroxide;† the copper is held in solution by the excess of ammonia. Filter off the precipitate and wash with dilute ammonia-water until the copper is completely removed. Dissolve the precipitate in hydrochloric acid and saturate this solution with hydrogen sulfide in the cold; selenium and tellurium together with arsenic, antimony, tin, and bismuth are thrown down as sulfides and are separated by filtration from the iron and phosphorus. Treat the precipitate thus obtained with sodium sulfide solution, and filter. The filtrate contains all the selenium and tellurium in the presence of arsenic, antimony, and tin as thio-salts. Make acid with nitric acid and carefully evaporate to dryness. Dissolve the residue in 200 ml of concentrated hydrochloric acid and treat as described on p. 272.

Molybdenum, Mo. At. Wt. 96.0

Form: Molybdenum Trioxide, MoO_3

If the molybdenum is present as ammonium molybdate, heat a weighed portion in a spacious porcelain or platinum crucible, at first carefully and later to a dull red heat; this leaves the molybdenum tri-

* *J. Am. Chem. Soc.*, **22**, 241.

† About 0.2 g of ferric iron should be present. If necessary, add some iron dissolved in nitric acid.

oxide behind in the form of a dense powder, appearing yellow when hot and almost white when cold. There is no danger of losing any of the molybdenum by volatilization, provided the dull red heat is not exceeded.

If the molybdenum is present as alkali molybdate, change it to mercurous molybdate or to its sulfide, and then analyze as described below.

Precipitation of Molybdenum as Mercurous Molybdate

In the course of analysis it is frequently necessary to determine molybdenum in alkali molybdates obtained by fusion with an alkali carbonate.

Neutralize the greater part of the alkali carbonate with nitric acid, and to the slightly alkaline solution add a barely acid solution of mercurous nitrate until no further precipitation is effected. Heat the liquid to boiling, allow the black precipitate, consisting of mercurous carbonate and mercurous molybdate, to settle, filter, and wash with a dilute solution of mercurous nitrate. Dry the precipitate, transfer as completely as possible to a watch glass, and dissolve the precipitate remaining on the filter in hot dilute nitric acid into a large porcelain crucible. Evaporate the solution to dryness, add the main portion of the precipitate to the residue, heat the whole very carefully over a low flame until the mercury is completely volatilized, and weigh the residual molybdenum trioxide.

Remark. — It was formerly customary to add a slight excess of mercurous nitrate solution and then to add mercuric oxide to neutralize the excess of nitric acid (the solution of mercurous nitrate contains free nitric acid). According to the above procedure of Hillebrand, the addition of mercuric oxide is wholly superfluous, for the basic mercurous carbonate suffices to remove the slight amount of free nitric acid.

Precipitation of Molybdenum as Molybdenum Sulfide

The precipitation of molybdenum as the sulfide can take place in two ways: either the acid solution may be precipitated by hydrogen sulfide gas, or the solution of ammonium thio-molybdate may be acidified with dilute acid.

(a) *Precipitation of Molybdenum Sulfide from Acid Solutions*

Place the molybdenum solution, slightly acid with sulfuric acid,* in a small pressure-flask and saturate in the cold with hydrogen sulfide.

* In some cases, *e.g.*, for the separation of Mo from Ba, Sr, and Ca, it is necessary to effect the separation in a *hydrochloric* acid solution.

Close the flask, heat on the water-bath until the precipitate has completely settled, and filter after it has become cold. Wash the precipitate with very dilute sulfuric acid and finally with alcohol until the acid has been completely removed. Place the moist filter in a large porcelain crucible and dry upon the water-bath. Cover the crucible and heat very carefully over a small flame until no more hydrocarbons are expelled. Then remove the cover, burn off the carbon from the sides of the crucible at as low a temperature as possible, and, by raising the temperature gradually, change the sulfide to oxide. The operation is finished when no more sulfur dioxide is formed. After cooling, add a little mercuric oxide suspended in water to the contents of the crucible, stir the mixture well, evaporate to dryness on the water-bath, remove the mercuric oxide by gentle ignition, and weigh the residue of molybdenum trioxide. The mercuric oxide helps to remove particles of unburned carbon.

It is much easier to transform the molybdenum trisulfide into the oxide as follows: Filter off the sulfide into a Gooch crucible, wash with water containing sulfuric acid, and then with alcohol, and dry at 100° C. Place the crucible within a larger nickel one, cover with a watch glass,* and carefully heat over a small flame whereby the sulfide is for the most part changed to the oxide. As soon as the odor of sulfur dioxide can no longer be detected, remove the watch glass and heat the open crucible to a constant weight. The molybdenum oxide thus obtained always contains traces of SO_3, and consequently has a bluish appearance. The results, nevertheless, are excellent.

(b) Precipitation of Molybdenum Sulfide from Alkaline Solution

To the molybdenum solution add an excess of ammonium hydroxide and saturate the solution with hydrogen sulfide until it assumes a bright-red color. Make acid with sulfuric acid and treat the precipitate as described under (*a*).

The Separation of Molybdenum from the Alkalies

can take place by precipitation as mercurous molybdate or as sulfide, as described above.

Separation of Molybdenum from the Alkaline Earths

Fuse the substance with sodium carbonate, extract the melt with water, and filter. The solution contains all the molybdenum as alkali

* To avoid loss by decrepitation.

molybdate, while the alkaline earths remain undissolved as carbonates. From the aqueous solution determine the molybdenum by one of the above methods.

Separation of Molybdenum from the Metals of the Ammonium Sulfide Group

Precipitate the molybdenum as sulfide (preferably from a sulfuric acid solution) by treatment with hydrogen sulfide under pressure (see p. 274). If the solution contains titanium, it is better to first add ammonia and ammonium sulfide, whereby the metals of Group III will be precipitated and the molybdenum will remain in solution in the form of its thio-salt. After filtration, precipitate the molybdenum as sulfide by the addition of acid (see p. 275, *b*).

Separation of Molybdenum from the Metals of Group II

(a) From Lead, Copper, Cadmium, and Bismuth

Make the solution alkaline with sodium hydroxide, add sodium sulfide, digest some time in a closed flask, and filter. The molybdenum remains in solution as its thio-salt, while the other metals are precipitated as sulfides. After filtering, acidify the solution with sulfuric acid and heat in a pressure-flask until the precipitate has settled and the supernatant liquid appears colorless. After allowing to cool, filter off the molybdenum sulfide and convert to oxide, as described on p. 275.

(b) From Arsenic

Add ammonium hydroxide to the solution, which must contain the arsenic as arsenic acid, and precipitate the arsenic by magnesia mixture (see p. 209), and filter. Make the filtrate acid with sulfuric acid and precipitate the molybdenum as sulfide as described on p. 274.

Separation of Molybdenum from Phosphoric Acid

Precipitate the phosphoric acid from the ammoniacal solution as magnesium ammonium phosphate (cf. Phosphoric Acid) and the molybdenum as sulfide in the filtrate (cf. p. 274, *a*). Another way is to saturate the ammoniacal solution with hydrogen sulfide, acidify with hydrochloric acid, and then precipitate the molybdenum as sulfide. In this filtrate precipitate the phosphoric acid as magnesium ammonium phosphate under the customary conditions.

Determination of Molybdenum as Lead Molybdate*

Weigh out 0.5–5.0 g of the finely powdered ore into a 250-ml Erlenmeyer flask (not more than 0.15 g of Mo or 0.25 g of MoS_3 should be taken), and heat with 15 ml of concentrated nitric acid until the brown fumes are gone. Then add 10 ml of concentrated hydrochloric acid and evaporate to a small volume. Add 15 ml of 18 N sulfuric acid and evaporate to fumes of sulfuric acid. Cool, add 50 ml of water, and boil gently for a few minutes. Filter into a 150-ml beaker. Wash the $PbSO_4$ and SiO_2 residue with hot water, then six to eight times with 4 N ammonia and finally with hot water.

If arsenic is present add a little ferric sulfate at this point to make sure that ten times as much iron as arsenic is present. Usually 0.3–0.4 g of the ferric salt is sufficient. This insures the precipitation of all the arsenic as ferric arsenate upon neutralization. Nearly neutralize the solution with ammonia, heat to boiling, and pour slowly into 75 ml of hot 9 N ammonia solution containing 3 g of sodium carbonate. The carbonate serves to precipitate alkaline earths if present. Stir well, and filter when the precipitate has settled. Wash with hot water. If arsenic is absent, omit the details described in this paragraph.

To the filtrate add 3 g of tartaric acid and saturate the alkaline solution with hydrogen sulfide. The tartaric acid is necessary to prevent the subsequent precipitation of vanadium and tungsten with the molybdenum. Filter off any precipitate that may form in this alkaline solution and wash with water containing hydrogen sulfide. To the filtrate add 6 N sulfuric acid until there is no further effervescence. Heat for a short time, filter off the MoS_3 precipitate, and wash with very dilute sulfuric acid saturated with hydrogen sulfide.

Dissolve this last sulfide precipitate in a little aqua regia and evaporate with hydrochloric acid to remove the nitric acid and the greater part of the excess acid. Dilute to 300 ml and neutralize with ammonia until alkaline to methyl orange. Then add 4–5 ml of 6 N hydrochloric acid, 10 g of ammonium acetate, and 2 ml of acetic acid. Heat to boiling and add 2 per cent lead acetate solution slowly from a buret, while stirring, until a drop of the solution tested on a spot plate will show no color change with fresh, 0.5 per cent tannin solution (cf. Volumetric Determination of Lead). A brown color is obtained before all the molybdenum has been precipitated. Next add 2–5 ml excess lead acetate and 5–10 ml of acetic acid. Heat on the hot plate nearly to boiling for 15–20 minutes, filter while hot, and wash with hot dilute ammonium nitrate solution. Ignite carefully and weigh as $PbMoO_4$.

* See U. S. Bur. Mines, Bull. 212, and Descriptive Circ. 6079.

Determination of Molybdenum in Steel

Dissolve 2–3 g of drillings or chips in 50 ml of 6 *N* nitric acid, evaporate to dryness, and heat in a porcelain dish until the ferric nitrate is well decomposed. During the heating the oxides are for the most part dislodged from the sides of the dish. Transfer the loose particles to an agate mortar, mix with 12 g of sodium peroxide, and transfer to a well-scoured nickel or iron crucible containing a little sodium peroxide on the bottom. Rub the dish, mortar, and spatula with more sodium peroxide and transfer the peroxide to the crucible. Finally add a little sodium hydroxide solution to the dish, heat nearly to boiling, rinse into a beaker, and set it aside.

Cover the crucible and heat with a small flame until the sodium peroxide melts, then raise the temperature and heat to dull redness for 15 minutes. Allow the crucible to cool, place it in a beaker, add 150 ml of hot water, and cover the beaker with a watch glass. The mass dissolves quickly and most of the excess peroxide is decomposed. Add the reserved alkaline solution, remove the crucible, washing it thoroughly, and heat the contents of the beaker for about an hour on the water-bath. If the solution then shows a green color due to manganate, or a purple color due to permanganate, cool, add a little more sodium peroxide, and stir. This serves to reduce manganate and permanganate to manganese dioxide. Dilute the solution to 200 ml, allow it to cool, and when well settled, decant the supernatant liquid through a filter. Wash twice by decantation with 50-ml portions of hot water and then on the filter until the washings are neutral to red litmus paper.

The insoluble residue may still contain a little molybdenum. Place the filter and its contents in the same crucible that was used before, heat till the carbon is consumed, and fuse with 8 g of a mixture of equal parts sodium carbonate and peroxide. Treat the melt as before and add the filtrate to that previously obtained.

If the molybdenum content is considerable (over 5 per cent) dilute in a calibrated flask and use an aliquot part for the molybdenum determination. Otherwise use the entire filtrate which contains, besides all the molybdenum, any vanadium, tungsten, phosphorus, silicon, etc., that was originally present.

Neutralize the greater part of the alkali with dilute sulfuric acid, evaporate to 100 ml, cool, and stir in 25 ml of concentrated ammonium hydroxide. Saturate the solution with hydrogen sulfide and continue as described on p. 266.

After adding the acid to precipitate MoS_3, it is well to introduce

hydrogen sulfide and heat while passing the gas to make sure that all the molybdenum is precipitated as sulfide.

Remarks. — If tungsten is present, add tartaric acid before adding sulfuric acid to the ammonium sulfide solution. This prevents the precipitation of tungsten sulfide.

If vanadium is present, the ignited molybdenum oxide has a dark color. After weighing the impure MoO_3 treat with sodium hydroxide solution and determine the vanadium volumetrically. Deduct the corresponding weight of V_2O_5 from that of the impure MoO_3.

If arsenic is present, remove it by adding magnesia mixture before introducing hydrogen sulfide.

The filtrate from the molybdenum sulfide precipitate will be violet or bluish green if chromium and vanadium are present: only part of the vanadium is precipitated with the molybdenum.

Pure molybdenum trioxide is light yellow when cold. On adding a drop of concentrated sulfuric acid and evaporating off the excess, a beautiful blue color is obtained. This test is very sensitive but may not be obtained if the molybdenum sulfide precipitate was not washed thoroughly to dissolve out sodium salts.

TUNGSTEN, W. At. Wt. 184.0

Tungsten is determined as its trioxide, WO_3.

If the tungsten is present as ammonium tungstate, as mercurous tungstate, or as tungstic acid, it can be changed by ignition in the air to yellow tungsten trioxide. Care should be taken not to heat strongly or some of the tungstic acid will be lost by volatilization. The crucible should be uncovered, and the full heat of the burner should not be used. When ignited over a Méker burner in a covered platinum crucible, a slow volatilization of tungstic acid takes place. There is danger of some tungsten being reduced by ignition of ammonium tungstate.

If the tungsten is present as alkali tungstate, the tungstic acid may be precipitated as such, or by means of mercurous nitrate as mercurous tungstate;* by ignition the yellow trioxide is obtained and weighed.

Precipitation of Tungstic Acid

Moisten the sample with 20 ml of concentrated hydrochloric acid, add 10 ml of concentrated nitric acid, and evaporate carefully to 10 or 15 ml. Rinse down the cover glass and sides of the container with water and dilute to about 150 ml. Add 5 ml of cinchonine hydrochloride solution (prepared by dissolving 12.5 g of cinchonine in 100 ml of $6N$

* See p. 179 for a method using tannin and cinchonine hydrochloride.

acid) and heat on the hot plate for 30 minutes or longer, stirring occasionally and keeping the temperature just below boiling.

Allow the tungstic acid to settle and then decant the solution through a filter containing some pulp made by digesting ashless filter paper with acid. Wash the precipitate 3 times with the above cinchonine hydrochloride solution diluted 100-fold. Transfer the precipitate to the filter and continue washing till free from alkali salt. Ignite at a low temperature in an open crucible and weigh the residual WO_3.

Remarks. — It is difficult to precipitate tungstic acid by simple evaporation with acid. Sodium tungstate, Na_2WO_4, unites to some extent with free tungstic acid to form an acid tungstate, $Na_2W_4O_{13}$ and this is not easily decomposed by acids. By heating with ammonium hydroxide the acid tungstate can be converted back to normal tungstate, but on adding acid some more of the acid tungstate is likely to form.

Cinchonine hydrochloride prevents the formation of the acid tungstate and also prevents the formation of colloidal solutions upon washing. During the ignition all the organic material is consumed so that the presence of cinchonine in the precipitate does no harm.

Tungstic acid is slowly volatilized by heating at a high temperature. The filter should be consumed at as low a temperature as possible and the heating stopped when the carbon is all gone.

Precipitation of Tungsten as Mercurous Tungstate

This method, proposed by Berzelius,* has often been used to precipitate tungsten from a solution of sodium tungstate obtained by fusion with alkali carbonate. As is true of phosphates, however, many tungstates are decomposed incompletely by fusion with sodium carbonate so that for the determination of tungsten in ores and in alloy steels it is better to decompose the material with acid and precipitate tungstic acid with the aid of cinchonine hydrochloride, as described above.

Procedure. — Add a few drops of methyl orange to the solution of alkali tungstate and add nitric acid till the indicator turns pink. Boil to expel carbonic acid, allow to cool, and add an excess of mercurous nitrate solution. The yellow precipitate settles quickly, and the supernatant liquid should appear as clear as water. After standing 3 or 4 hours, filter off the precipitate, wash with water containing mercurous nitrate (5 ml saturated mercurous nitrate solution diluted with water to 100 ml), dry, ignite in a porcelain crucible under a good hood, using the flame of a Bunsen burner, and weigh as WO_3.

Precipitation of Tungsten as Benzidine Tungstate†

If a neutral solution of sodium tungstate is treated with benzidine hydrochloride, a white flocculent precipitate of benzidine tungstate is

* *Jahresber.*, **21**, II, 143. Cf. O. v. der Pfordten, *Ann.*, **222**, 152 (1883).

† G. v. Knorre, *Ber.*, **38**, 783 (1905).

formed and the precipitate is insoluble in water containing benzidine hydrochloride; when formed in the cold it is hard to filter and, on being washed with pure water, tends to run through the filter. If the precipitate is formed from a hot solution, however, it comes down in a more compact condition and after cooling* can be easily filtered and washed without loss with water containing benzidine hydrochloride. The moist precipitate on being heated to 800° yields a residue of WO_3.

The precipitation can also take place satisfactorily from a cold solution if, before adding the precipitant, a little dilute sulfuric acid or alkali sulfate is added to the solution. In this case a mixture of crystalline benzidine sulfate and amorphous benzidine tungstate is formed which can be filtered after standing 5 minutes. The benzidine sulfate is entirely volatile, so that equally good results are obtained by either of the above two procedures.

If the tungsten is present as tungstate after fusing with sodium carbonate, dissolve the melt in water, add a little methyl orange to the clear solution, then hydrochloric acid until the pink color is obtained, and finally 10 ml of 0.1 *N* sulfuric acid. Benzidine hydrochloride gives a precipitate which can be filtered in 5 minutes. Wash with dilute benzidine hydrochloride until the evaporation of a few drops of the filtrate on platinum foil leaves no weighable residue. Ignite the moist precipitate as described above.

Preparation of the Benzidine Solution

Triturate 20 g of commercial benzidine in a mortar with water, wash into a beaker with about 400 ml of water, treat with 25 ml hydrochloric acid (*d.* 1.2), and heat until solution is complete and a brown liquid is formed. Filter and dilute to 1 l. Of this solution, 5.6 ml is sufficient to precipitate 0.1 g of WO_3.

If the analysis is carried out in the presence of sulfuric acid, it is necessary to add at least 1 ml of the benzidine solution for 10 ml of 0.1 *N* sulfuric acid added.

Preparation of the Wash Liquid

Dilute 10 ml of the above solution with distilled water to a volume of 300 ml.

* Since benzidine tungstate is appreciably soluble in hot water containing benzidine hydrochloride, it is necessary in all cases to postpone the filtration until the solution is cold.

Determination of Tungsten in Chrome-Tungsten Steel*

Procedure. — Treat 1.0 g of the steel in a 400-ml beaker with 50 ml of concentrated HCl, and heat in the covered beaker until all the metal is decomposed. Remove from the heat and add cautiously 5 to 7 ml of concentrated HNO_3. Cover the beaker, and boil for 5 minutes to oxidize all the iron and convert the tungsten to yellow tungstic acid. Remove from the heat, wash the under part of the watch glass and the sides of the beaker with hot water, dilute to 75–100 ml, and filter through a 9-cm ashless filter containing some filter-paper pulp made from ashless filters. Wash the precipitate alternately, three times each, with 10-ml portions of hot 6 *N* HCl and hot water, and finally with four similar portions of hot water. Transfer the paper and precipitate to a weighed platinum crucible, ignite, and weigh. Treat the impure WO_3 with sulfuric and hydrofluoric acids (see Silicic Acid) to volatilize SiO_2, and call the residue WO_3.

Remark. — Sometimes the WO_3 is quite impure and should be subjected to the following treatment: Fuse the impure tungstic acid with sodium carbonate, dissolve the melt in water, filter off the ferric oxide and chromic oxide, wash thoroughly, return to the thoroughly washed crucible, and ignite. Repeat the fusion with a small amount of sodium carbonate, filter, wash, ignite, and weigh. Deduct this weight from that of the impure tungstic acid.

Sometimes a little chromium is present in the impure tungstic acid. In that case the aqueous extract of the fusions will be yellow and the chromium content can be estimated by the depth of color.

Determination of Tungsten in Ores †

Procedure. — Weigh out accurately about 1 g of the finely ground ore into a 400-ml beaker. Moisten the sample with 5 ml of water and add 100 ml of concentrated hydrochloric acid. Cover the beaker and digest at about 60° for at least an hour. Stir from time to time to prevent the formation of any crust. Then evaporate slowly to about 50 ml. Add 40 ml more of strong hydrochloric acid, 20 ml of concentrated nitric acid and evaporate to about 10 ml. During these operations, especially when fresh acid is added, stir the material at the bottom of the beaker so that it does not become encrusted.

Rinse down the cover glass and the sides of the beaker and dilute with water to about 150 ml. If, by accident, the solution was evaporated to dryness during the above treatment, add 20 ml of concentrated hy-

* This method has been recommended by the Bureau of Standards at Washington, D. C.

† Recommended by J. A. Holliday and found satisfactory by collaborative work in 17 different laboratories in 1918 under the direction of W. F. Hillebrand.

drochloric acid and 10 ml of concentrated nitric acid to the residue and evaporate to 10 or 15 ml.

To the diluted solution add 5 ml of cinchonine hydrochloride solution (12.5 g of cinchonine dissolved in 100 ml of 6 N hydrochloric acid) and heat on the hot plate for 30 minutes or longer. The solution should be at a temperature just below the boiling point and should be stirred occasionally.

Allow the tungstic acid anhydride to settle and then decant the solution through a filter which contains some pulp made by digesting ashless filter paper with acid. Wash the precipitate three times with a solution containing 10 ml of the above cinchonine solution to a liter of hot water. Then transfer the precipitate to the filter and wash with this same, diluted cinchonine solution.

Wash the tungstic anhydride back into the original beaker by a jet of water, using about 25 ml to accomplish this. Add 6 ml of concentrated ammonia solution and heat gently, with the beaker covered, for about 10 minutes to convert all the tungstic acid into ammonium tungstate. Rinse down the sides of the beaker with hot, dilute ammoniacal ammonium chloride solution (200 ml of concentrated ammonia, 800 ml of water, and 10 ml of concentrated hydrochloric acid). Stir up the contents of the beaker and filter through the same filter that was used for the previous filtration. Collect the filtrate in a 400-ml beaker and wash the original beaker and filter with the hot ammoniacal solution. The presence of a little ammonium chloride in this ammoniacal solution prevents colloidal silicic acid from passing into the filtrate.

The residue on the filter is usually free from tungsten, but it should be tested by giving it the same treatment as that of the original ore. Ammonium and sodium salts tend to prevent the complete precipitation of tungstic acid, so that it is important, next, to remove the excess ammonia. After this has been evaporated off, add 20 ml of concentrated hydrochloric acid and 10 ml of concentrated nitric acid and evaporate to about 15 ml. Dilute with 150 ml of water and precipitate the remainder of the tungstic acid by treatment with cinchonine solution as described above.

After filtering and washing the precipitate as before, ignite it carefully in a weighed platinum crucible. The presence of the paper pulp causes the precipitate to form a porous, friable mass and makes it easy to oxidize the carbon. If the ignition is made in a muffle, the introduction of oxygen is advantageous. After burning off the carbon, at as low a temperature as possible, weigh the precipitate and correct for silica by the usual treatment with hydrofluoric acid p. 289.

If the tungstic acid is heated over the full flame of the burner, some

of it will be lost by volatilization. After the removal of the silica, the residue should be heated to dull redness for only 1 minute. Heated in the muffle, the maximum temperature should not exceed 800°. The ignited tungsten trioxide, WO_3, should have a clean, lemon-yellow color.

To test for tungsten in the residue that is insoluble in ammonia, ignite it in an iron crucible and fuse the ash with a small quantity of sodium peroxide mixed with a little sodium carbonate. Reducible metals are likely to ruin a platinum crucible if the residue and filter paper are heated in it. Extract the melt with water and filter. Acidify the aqueous extract with hydrochloric acid, add 5 ml of cinchonine hydrochloride solution, and heat for several hours to see if any yellow tungstic acid anhydride is formed.

Rapid Method for Determining Tungsten in Ores

Treat 1 g of ore in a platinum dish with about 10 ml of HF, 25 ml of concentrated HCl, and 10 ml of 9 *N* $HClO_4$. Heat carefully until the sample is decomposed, adding more HF if necessary. Evaporate on an air-bath to fumes of $HClO_4$. Dilute with water and transfer to a 400-ml beaker. The WO_3 can usually be removed from the dish by rubbing with a rubber policeman. If any stain adheres, dissolve it in a little concentrated ammonia and add to the acid solution. Add 75 ml of concentrated HCl and 25 ml of concentrated HNO_3, and evaporate to about 20 ml at a temperature a little below the boiling point. Dilute with 100 ml of cold water add 10 ml of cinchonine, and allow 2 hours for the precipitate to settle.* Filter and wash with dilute cinchonine solution as described on p. 283. Ignite the residue in a weighed platinum crucible to a dull red heat and weigh. Treat with HF and H_2SO_4 as described on p. 289 to make sure that the original treatment removed all SiO_2.

Separation of Molybdenum from Tungsten

(*a*) *The Sulfuric Acid Method*

This method, proposed by M. Ruegenberg and E. F. Smith,† depends upon the fact that unignited molybdic acid is readily dissolved by warming with sulfuric acid (*d.* 1.38), while tungstic acid is not.

* The above procedure is essentially that recommended by Ledoux and given in Bull. 212 of the Bureau of Mines. Ledoux recommends fusing the final precipitate with sodium carbonate as described on p. 282. George W. Muller tested the above procedure and found such correction apparently unnecessary in the analysis of Scheelite. Muller found it advantageous to use the centrifuge instead of waiting 2 hours for the final WO_3 precipitate to settle.

† *J. Am. Chem. Soc.*, **22**, 772.

W. Hommel* tested this method in the author's laboratory, and could not obtain good results except by digesting the moist oxides with *concentrated* sulfuric acid, and afterward diluting with three times as much water.

Procedure. — (α) Both acids are present in a moist, freshly precipitated state.

Cover the mixture with concentrated sulfuric acid in a porcelain dish and heat over a free flame. By this means, usually a small amount of the tungstic acid is oxidized to the blue oxide, so that the yellow precipitate of tungstic acid is tinted with green. On adding one or two drops of dilute nitric acid, the green color disappears and the tungstic acid is of a pure yellow color. After digesting for half an hour, the separation is complete. Cool, dilute the liquid with three times its volume of water, filter, wash with water containing sulfuric acid, then two or three times with alcohol, ignite (after burning the filter by itself) in a porcelain crucible, and weigh as WO_3.

Precipitate the molybdenum in the filtrate by passing hydrogen sulfide into the sulfuric acid solution in a pressure-flask, and treat the precipitate as described on p. 275.

If only a little sulfuric acid is used for the separation, the filtrate from the tungstic acid can be evaporated in a platinum dish, the sulfuric acid driven off for the most part, and the residue washed into a weighed platinum crucible with ammonia, and then evaporated, ignited, and weighed. If large amounts of molybdenum are present, however, it is always safer to precipitate the molybdenum as sulfide.

(β) *Tungsten and Molybdenum are Present in the Form of Their Ignited Oxides*

These ignited oxides cannot be separated by treatment with sulfuric acid. According to W. Hommel, they can readily be brought into solution by heating for half an hour on the water-bath with concentrated ammonia in a pressure-flask, shaking frequently.

After cooling, wash the contents of the flask, whether dissolved or not, into a porcelain dish, evaporate to dryness, and treat as described under (α).

It is still better to fuse the ignited oxides with four times as much sodium carbonate, and treat the melt as described under (α).

(*b*) *Sublimation Method*†

If a mixture of the trioxides of tungsten and molybdenum, or of their alkali salts, is heated at 250–270° in a current of dry hydrochloric acid, the molybdenum is

* *Inaug. Dissert.*, Giessen, 1902.

† Péchard, *Compt. rend.*, **114**, p. 173, and **46**, p. 1101.

volatilized completely as $MoO_3 \cdot 2HCl$, which collects on the cooler parts of the tube as a beautiful, white, wool-like sublimate, while the tungsten trioxide remains behind in the boat.

Procedure. — Weigh out about 0.3 g of the oxides of the two elements, or their sodium salts, into a porcelain boat, and place the boat in a tube made of difficultly fusible glass, of which one end is bent vertically downward and is connected with a Péligot tube containing a little water. Insert the horizontal arm of the tube through a drying-oven (to serve as an air-bath) (see Fig. 28, p. 48), and connect with an apparatus for generating hydrogen chloride gas. Pass this gas through a flask containing concentrated hydrochloric acid, and then through concentrated sulfuric acid. As soon as the temperature has reached about 200° the sublimation of the molybdenum begins. From time to time drive over the sublimate that collects in the combustion tube toward the Péligot tube* by carefully heating with a free flame, to see whether any more molybdenum is being volatilized. After heating for 1.5–2 hours, the operation is usually complete. Remove the boat containing tungsten trioxide, or the latter with sodium chloride, and if only the former is present, weigh after drying in a desiccator over caustic potash. If, however, sodium chloride is present (when the tungsten was originally present as sodium tungstate) remove this by treatment with water, and weigh the filtered WO_3.

For the determination of the molybdenum, wash out the sublimate in the tube by means of water containing a little nitric acid, and carefully evaporate the nitric acid solution of the entire sublimate to dryness in a porcelain dish. Dissolve the residue in ammonia, wash into a porcelain crucible, evaporate to dryness, and change to MoO_3 by gentle ignition.

(*c*) *The Tartaric Acid Method of H. Rose*

To the aqueous solution of the alkali salts of the two metals add considerable tartaric acid and an excess of sulfuric acid. Precipitate the molybdenum according to p. 274, by hydrogen sulfide in a pressure-flask. Filter off the molybdenum sulfide and change by roasting in the air to the trioxide. For the determination of the tungsten, destroy the tartaric acid by repeated evaporation with nitric acid, filter off the precipitated tungstic acid and change by ignition to the trioxide.

* By the absorption of the $MoO_3 \cdot 2HCl$ in the water of the Péligot tube, the brick-red acid chloride, $Mo_3O_5Cl_8$, is often formed:

$$3[MoO_3 \cdot 2HCl] + 2\ HCl = 4\ H_2O + Mo_3O_5Cl_8$$

This substance is insoluble in hydrochloric acid, but readily soluble in nitric acid.

Remark. — This method gives correct results, but is not so satisfactory as the preceding one on account of the time consumed in removing the tartaric acid.

Analysis of Tungsten Bronzes

The analysis of these alkali salts of complex tungsten acids, discovered by Wöhler in 1824,* offered for a long time considerable difficulty on account of the fact that acids do not decompose them very readily.

By fusion with alkalies in the air, or better still in the presence of potassium nitrate, the tungsten bronzes can be converted without difficulty into normal alkali tungstate, and the tungsten determined by one of the methods already described. It is obvious that the alkalies cannot be determined in the same sample, so that Philipp† proceeded as follows:

Treat the bronze with ammoniacal silver nitrate solution. The WO_2 is thereby oxidized to WO_3 and an equivalent amount of silver is precipitated, but the whole of the tungsten remains in solution in the form of alkali and ammonium tungstates. In the filtrate obtained after filtering off the deposited silver, precipitate the tungstic acid by treatment with nitric acid and determine as WO_3. After removing the excess of silver, by precipitating it as the chloride, evaporate the filtrate to dryness with the addition of sulfuric acid, and weigh the alkali as sulfate.

Although the above method affords satisfactory results in the analysis of bronzes containing comparatively little tungsten, it is wholly inadequate in the case of bronzes rich in tungsten. The method of Brunner,‡ which follows, is applicable in all cases. It is based upon the fact that the bronzes can be transformed very easily, and without loss of alkali, into normal tungstates by heating with ammonium persulfate, or ammonium acid sulfate.

Procedure. — Treat 0.5 g of the finely powdered bronze in a porcelain crucible with 2 g of alkali-free ammonium sulfate and 2 ml of concentrated sulfuric acid,§ heating carefully over a small flame. During the heating frequently shake the contents of the crucible about a little by cautiously moving the crucible. The escape of gases from the crucible soon ceases and when sulfuric acid vapors begin to be evolved, the decomposition of the bronze results.

With sodium and lithium bronzes, the fused mass appears greenish, whereas with a potassium bronze the color is yellowish white. After a part of the ammonium sulfate has been volatilized, allow the mass in the crucible to cool, add another gram of ammonium sulfate and 1 ml of concentrated sulfuric acid. Again heat the contents of the crucible as before until sulfuric acid fumes come off thickly; then allow the crucible to cool.

* *Pogg. Ann.*, **2**, 350.

† *Ber.*, **15**, 500 (1882).

‡ *Inaug. Dissert*, Zürich, 1903.

§ If ammonium persulfate is used the addition of sulfuric acid is unnecessary. The only objection to the use of the persulfate lies in the fact that the commercial salt often contains some potassium persulfate.

Soften the greenish or yellowish white residue by treatment with water and rinsing into a porcelain dish. After adding 50 ml of concentrated nitric acid, digest the contents of the evaporating dish on the water-bath for 3 or 4 hours, and then, after diluting with water, filter off the residue of pure yellow tungstic acid.

To recover the small amount of tungstic acid remaining in the filtrate, evaporate as far as possible on the water-bath, allow to cool, dilute with a little water, carefully treat with an excess of ammonia, again evaporate on the water-bath, and treat as described on p. 279.

Evaporate the final filtrate from the tungstic acid determination to dryness, expel ammonium salts by ignition and weigh the residue of alkali sulfate (cf. pp. 57 and 58).

Separation of Tungsten from Tin*

Mix 1 g of the finely powdered mineral in an iron crucible with 8 g of sodium peroxide, and carefully fuse the mixture over a Bunsen burner for about 15 minutes. After cooling, soften the melt with water and transfer into a 250-ml flask (if lead is present, conduct carbon dioxide into the solution for a few minutes), dilute the solution to the mark, mix well and filter through a dry filter, rejecting the first few milliliters of the filtrate.

For the determination of the tungstic acid, take 100 ml of the filtrate and proceed as described on p. 279.

For the determination of the tin, use a second 100 ml of the original alkaline solution. Treat with 45 ml of concentrated hydrochloric acid, to precipitate tungstic and stannic acids. Add 2 or 3 g of pure zinc to change the tungstic acid to the blue oxide and reduce the stannic acid to metallic tin. Allow the mixture to stand quietly for an hour at a temperature between 50° and 60°. The tin then goes into solution as stannous chloride, and the greater part of the tungsten remains undissolved in the form of the blue oxide. Filter off the latter, and wash. In this way the whole of the tin should be obtained in an acid solution, in the presence of a small amount of tungsten, which does no harm. Dissolve the blue oxide on the filter, however, in hot, dilute ammonia solution to make sure that it contains no trace of metallic tin. If it does, dissolve the small particle of tin in a little hydrochloric acid and add the resulting solution to the main solution of the tin.

Now dilute the solution with water and precipitate the tin as stannous sulfide by introducing hydrogen sulfide gas. Filter off the precipitate, ignite in a porcelain crucible and weigh as SnO_2 (see p. 226). Or

* Cf. H. Augenot, *Z. angew. Chem.*, **19**, 140 (1906).

dissolve the moist precipitate of stannous sulfide in potassium hydroxide solution and determine tin by electrolysis (see p. 227).

According to Donath and Müller* a mixture of stannic oxide and tungstic acid may be separated as follows: Ignite the mixture with powdered zinc for 15 minutes in a covered porcelain crucible. After cooling, heat the spongy mass in the crucible in a beaker with $4N$ hydrochloric acid (1:2) until evolution of hydrogen is no longer perceptible. Allow the solution to cool somewhat and add powdered potassium chlorate little by little until the blue tungsten oxide is completely transformed to yellow tungstic acid, and the liquid no longer shows any blue tinge. Dilute with $1\frac{1}{2}$ times as much water, and after standing 24 hours filter off the tungstic acid, washing the precipitate first with dilute nitric acid and then with 1 per cent solution of ammonium nitrate. Dry, ignite, and weigh as WO_3. Determine the tin in the filtrate as above.

Separation of Tungstic Acid from Silica

When a mixture of tungstic and silicic acid is at hand, such as is obtained by evaporation with nitric acid, the silicic acid may be removed by treating the ignited residue with hydrofluoric acid and a large excess of sulfuric acid. The separation does not succeed, however, in the mixture of oxides as obtained after precipitation with mercurous nitrate, for the silicic acid is so enveloped with tungstic acid that some of the former is not volatilized as fluoride. In such cases, as Friedheim† has shown, excellent results may be obtained by the

Method of Perillon‡

Place the mixture of ignited oxides in a platinum boat and heat to redness in a stream of dry hydrogen chloride. Thereby the tungsten is volatilized, probably as an acid chloride, which can be recovered in a receiver containing dilute hydrochloric acid; the silica remains behind in the combustion tube.

Frequently the tungsten is reduced to a blue lower oxide, which is not volatile in a current of hydrochloric acid gas. In such cases, after the apparatus has been allowed to cool, replace the hydrogen chloride by air, and heat the contents of the boat in a current of air. Again allow the tube to cool, replace the air by hydrogen chloride, and once more heat the tube to redness. Repeat the process if necessary until finally a

* *Wiener Monatsh.*, **8**, 647 (1887).

† *Z. anorg. Chem.*, **45**, 398 (1905).

‡ *Bull. soc. l'industrie miner.*, 1884.

residue of pure white SiO_2 is obtained. Evaporate the tungstic acid hydrochloride in the receiver to dryness with nitric acid, filter off the precipitated WO_3, ignite and weigh. Unless the current of hydrogen chloride gas is perfectly free from air, the platinum boat will be strongly attacked.

VANADIUM, V. At. Wt. 50.95

Vanadium is determined as the pentoxide, V_2O_5. The most convenient method for determining vanadium is a volumetric process, and will be discussed in the chapter on Volumetric Analysis.

If vanadium is present as ammonium or mercurous vanadate, it can be easily changed to the pentoxide by ignition; the latter is a reddish brown fusible substance which solidifies as a radiating, crystalline mass. If vanadic sulfide is carefully roasted in the air, it is also changed quantitatively to the pentoxide.

In the analysis of most minerals containing vanadium, the vanadium is separated from the other metals present by fusing with a mixture of six parts sodium carbonate and one part potassium nitrate. After cooling, the melt is extracted with water, whereby the sodium vanadate goes into solution while most of the metals are left behind in the form of oxides or carbonates. If phosphorus, arsenic (molybdenum, tungsten), and chromium are present, these elements also dissolve on treating the melt with water in the form of the sodium salts of the corresponding acids.

In practice, therefore, the vanadium is usually met with as the sodium salt of vanadic acid, and it is a matter of separating it from the aqueous solution obtained after fusing with sodium carbonate and potassium nitrate, and of separating it from the other acids which are likely to accompany it (phosphoric, arsenic, and chromic acids).

Precipitation of Vanadic Acid from the Solution of Sodium Vanadate

There are two good methods for the separation of vanadic acid from a solution of an alkali vanadate: the Rose method, according to which the vanadium is precipitated as mercurous vanadate, and that of Roscoe, by which it is precipitated as lead vanadate. The Berzelius-Hauer method,* in which the vanadium is precipitated as ammonium metavanadate, was found by Holverscheidt† to give low results, but Gooch and Gilbert,‡ as well as E. Campagne,§ obtained correct results by

* *Pogg. Ann.*, **22**, 54 and *J. prakt. Chem.*, **69**, 388.

† *Dissertation*, Berlin, 1890.

‡ *Z. anorg. Chem.*, **32**, 175 (1902).

§ *Ber.*, **1903**, 3164.

working in an ammoniacal solution, which was saturated with ammonium chloride.

1. *The Mercurous Nitrate Method of Rose*

Nearly neutralize the alkaline solution with nitric acid and then add, drop by drop, a nearly neutral solution of mercurous nitrate* until, after the precipitate has settled, a further addition of the reagent causes no precipitation. Heat to boiling, allow the gray-colored precipitate to settle, filter and wash with water containing a few drops of mercurous nitrate solution. Ignite under a good hood, and weigh the residue of V_2O_5.

Remark. — In neutralizing the alkaline solution of the vanadate with nitric acid, the solution must on no account be made acid, for then nitrous acid (from the nitrate fusion) will be set free and the nitrous acid reduces some of the vanadate to a vanadyl salt which is not precipitated by mercurous nitrate. In order to avoid passing over the neutral point, Hillebrand recommends fusing with a weighed amount of sodium carbonate and adding the amount of nitric acid that has been found necessary by a blank test to neutralize this. The method gives good results, but under these conditions chromate, molybdate, arsenate, tungstate and phosphate will be precipitated so that it is useful only in the absence of chromium, molybdenum, tungsten, etc. The same is true of the following method of Roscoe.

2. *The Lead Acetate Method of Roscoe*†

Principle. — If a solution weakly acid with acetic acid is treated with lead acetate, orange-yellow lead vanadate is precipitated quantitatively. The lead vanadate, however, does not possess a constant composition, so that the amount of vanadium present cannot be determined by weighing the precipitate. After being washed, it is dissolved in as little nitric acid as possible, the lead precipitated as lead sulfate, and the vanadium determined in the filtrate by evaporating the latter, driving off the excess of sulfuric acid, and weighing the residual V_2O_5.

Procedure. — Nearly neutralize the solution from the sodium carbonate and potassium nitrate fusion with nitric acid as described in the previous method. Stir in it an excess of lead acetate solution; the voluminous precipitate will soon coagulate and settle to the bottom of the beaker leaving a perfectly clear supernatant liquid. The precipitate is at first orange-colored, but on standing it gradually becomes yellow and finally perfectly white. Filter and wash with water containing acetic acid until a little of the filtrate will leave no residue on evaporation. Wash the precipitate into a porcelain dish, dissolve the part remaining on the filter in as little as possible of hot, dilute nitric acid, and add the solution to the main part of the precipitate, to which add enough

* The mercurous nitrate should leave no residue on being heated strongly.

† *Ann. Chem. Pharm., Suppl.*, 8, 102 (1872).

nitric acid to dissolve it completely. Then add an excess of sulfuric acid, evaporate on the water-bath as far as possible, and finally heat over a free flame until dense fumes of sulfuric acid are evolved. After cooling, add 50–100 ml of water, filter off the lead sulfate, and wash with dilute sulfuric acid until 1 ml of the filtrate will show no yellow color with hydrogen peroxide. The lead sulfate should be white and free from vanadium; it will be so provided enough sulfuric acid was used and the mass was not heated until absolutely dry before diluting with water. Evaporate the filtrate containing all the vanadic acid in a porcelain dish to a small volume, transfer to a weighed platinum crucible, evaporate further on the water-bath, and finally in an air-bath until all the sulfuric acid is removed. Ignite the contents of the open crucible for some time* at a faint-red heat and finally weigh as V_2O_5.

Remark. — Instead of decomposing the lead vanadate by means of sulfuric acid, Holverscheidt recommends precipitating the lead as sulfide by means of hydrogen sulfide and determining the vanadium in the filtrate. For this purpose boil the blue-colored filtrate from the lead sulfide precipitate (which contains some vanadyl salt) to expel the excess of hydrogen sulfide and filter off the deposited sulfur. Add a few drops of nitric acid, evaporate the solution to dryness, and change the reddish yellow hydrate of vanadic acid by gentle ignition into the pentoxide of vanadium.

Lead may also be separated from the vanadic acid as lead chloride. In this case the procedure recommended on p. 241 is followed.

The separation of vanadium as the sulfide by acidifying a solution of an alkali vanadate that has been treated with an excess of ammonium sulfide is not admissible, for only a part of the vanadium is precipitated as the brown sulfide, the rest remaining in solution in the form of vanadyl salt. H. Rose called attention to the inaccuracy of this method, but this has not prevented its being recommended in some works on analytical chemistry. The author has carefully tested the method and found it useless.

Separation of Vanadium from Arsenic Acid

Most minerals containing vanadium also contain arsenic, and after extracting the melt, obtained by fusion with sodium carbonate and niter, *with water*, both elements go into solution. For their separation, make the solution acid with dilute sulfuric acid and introduce sulfur dioxide into the hot liquid; the vanadic acid is reduced to vanadyl salt and the arsenic to arsenious acid. After boiling to remove the excess of sulfur dioxide, saturate the solution with hydrogen sulfide and filter off the precipitate of arsenic trisulfide. Remove hydrogen sulfide from the filtrate by boiling, evaporate with nitric acid to form vanadic acid again, make the solution alkaline with sodium carbonate, and determine the vanadium by one of the above methods.

* On expelling the sulfuric acid, there are finally formed some green and brown crystals of a compound of vanadic acid with sulfuric acid; these are decomposed only at a faint-red heat.

Separation of Vanadium from Phosphoric Acid

If the aqueous solution obtained after the soda-niter fusion contains phosphoric as well as vanadic acid, both are precipitated by mercurous nitrate. By igniting and weighing the washed precipitate the sum of the $V_2O_5 + P_2O_5$ is obtained. When P_2O_5 is present the V_2O_5 does not melt, but only sinters together. Fuse the ignited oxides with an equal weight of sodium carbonate, dissolve the melt in water, make the solution acid with sulfuric acid and boil with sulfurous acid to reduce the vanadic acid to vanadyl sulfate; the latter will be recognized by the pure blue color which the solution assumes. Pass carbon dioxide into the boiling solution until the excess of sulfurous acid is removed, and then allow to cool. To the cold solution, now about 100 ml in volume, add 200 ml of a 75 per cent solution of ammonium nitrate and 50 ml of ammonium molybdate solution (cf. Remark, below). Heat the solution to about 60°, set aside and allow to stand for 1 hour. Decant the clear liquid through a filter, and wash three times by decantation with 50 ml of the proper wash liquid (see Phosphoric Acid). Dissolve the precipitate by pouring 10 ml of 8 per cent ammonia through the filter into the beaker containing the bulk of the precipitate and finally wash the filter with 30 ml of water. To this solution add 20 ml of a 34 per cent ammonium nitrate solution and 1 ml more of ammonium molybdate, heat just to boiling, and reprecipitate the phosphoric acid by the addition of 20 ml of hot 25 per cent nitric acid. Determine the phosphoric acid by the method of Woy (see Phosphoric Acid). Deduct the amount of P_2O_5 found from the sum of the oxides to get the weight of V_2O_5.

Remark. — A. Gressly tested this method in the author's laboratory and made the interesting observation that if about 0.15 g of V_2O_5 was present with 0.1 g P_2O_5, no trace of the latter could be detected according to the procedure of Woy, not even on boiling the solution. On the other hand, an immediate precipitation was produced if a stronger solution of ammonium molybdate were used (75 g of ammonium molybdate dissolved in 500 ml of water) and this solution poured into 500 ml of nitric acid, *d.* 1.2.

The above-described separation gives correct results only when the vanadium is present as vanadyl sulfate; if vanadic acid is present it is precipitated with the phosphoric acid. If the solution is allowed to stand after the addition of the ammonium molybdate, the vanadyl sulfate is gradually oxidized to vanadic acid; the precipitate therefore should not be allowed to stand long before filtering.

Separation of Vanadium from Molybdenum

Precipitate the molybdenum as sulfide from sulfuric acid solution by the action of hydrogen sulfide under pressure as described on p. 274. Ignite and weigh as MoO_3.

Boil off hydrogen sulfide from the filtrate and determine vanadium as described under the Separation of Vanadium from Arsenic Acid on p. 292.

Determination of Vanadium and Chromium in Iron Ores and Rocks

As vanadium often occurs in many ores of iron and in rocks, although in very small amounts, it is often of interest and of importance to be able to determine it in such cases. For this purpose, W. F. Hillebrand* proceeds as follows:

Fuse 5 g of the finely powdered mineral with 20 g sodium carbonate and 3 g potassium nitrate over the blast lamp. Extract the fused mass with water, add a few drops of alcohol to reduce the green manganite, and filter off the residue.†

The aqueous solution contains sodium vanadate and often phosphate, chromate, molybdate, aluminate, and considerable silicate as well. First of all, remove the aluminum and the greater part of the silicic acid by nearly neutralizing the alkaline solution with nitric acid.‡ It is very important not to make the solution acid at this point on account of the reducing action of the nitrous acid set free from the nitrite formed during the fusion. Evaporate the nearly neutral solution to approximate dryness, take up in water, and filter.§

Treat the cold alkaline solution with an almost neutral solution of mercurous nitrate until no further precipitation takes place. The somewhat voluminous precipitate contains, besides mercurous carbonate, also mercurous chromate, vanadate, molybdate, arsenate, and phosphate, if the corresponding elements are present in the mineral. If the precipitate is too bulky, cautiously add a little nitric acid, and then a drop of mercurous nitrate in order to see if the precipitation is complete.

Heat the liquid to boiling, filter, wash the precipitate with water containing ammonium nitrate, dry, and ignite in a platinum crucible at as low a temperature as possible. Fuse the ignited residue with a little sodium carbonate, extract the melt with water and, if yellow-colored, filter into a 25-ml flask and determine the amount of chromium colori-

* *U. S. Geol. Survey Bull.*, 700.

† If considerable vanadium is present, the insoluble residue may contain vanadium and should be fused with soda and niter again.

‡ Determine the amount of nitric acid necessary to neutralize 20 g of sodium carbonate by a blank test.

§ The residue of aluminum hydroxide and silicic acid rarely contains vanadium, but often does contain chromium. If it is desired to determine the chromium, evaporate the residue to dryness with hydrofluoric and sulfuric acids, fuse the dry mass with soda and niter again, and add the aqueous solution of the melt to the main solution.

metrically by comparing its color with a carefully prepared solution of potassium chromate.

Then slightly acidify the solution with sulfuric acid, and precipitate the molybdenum, arsenic, and traces of platinum by hydrogen sulfide in a pressure-flask. Filter off the precipitated sulfides, carefully ignite the filter together with the precipitate in a porcelain crucible, add a few drops of sulfuric acid and heat the crucible again until the acid is almost completely removed. On cooling the mass is colored a beautiful blue if molybdenum is present.

Expel hydrogen sulfide from the filtrate by boiling and introducing carbon dioxide at a volume of not over 100 ml. Then titrate the *hot* solution to a pink color with $0.01\,N$ potassium permanganate solution (cf. Volumetric Analysis). To obtain absolutely accurate results, reduce the hot solution again with sulfur dioxide, expel the excess with carbon dioxide and repeat the titration. This result is usually a trifle lower and should be taken as correct.

$$5\,V_2O_2(SO_4)_2 + 2\,KMnO_4 + 22\,H_2O = 2\,KHSO_4 + 2\,MnSO_4 + 10\,H_3VO_4 + 6\,H_2SO_4$$

This method gives correct results only when the amount of chromium present is very small, which it usually is.

If more than 5 mg of chromium is present a correction must be made, for a measurable amount of permanganate is used up in oxidizing the chromium. This is determined by taking a solution containing the same amount of chromate as the analyzed solution, reducing it with sulfurous acid, and titrating with permanganate. The amount of permanganate now used must be subtracted from the amount used in the analysis, and from the difference the amount of vanadium can be calculated.

Determination of Vanadium and Molybdenum in Steel

*Modified Method of A. A. Blair**

Dissolve 2 g of the steel in 50 ml $6\,N$ nitric acid, evaporate to dryness, and bake the residue to decompose nitrates. Take up with hydrochloric acid and carry out the Rothe ether separation as described on p. 173. Practically all of the molybdenum will be dissolved in the ether, and all the chromium, vanadium, and nickel will be in the aqueous acid solution.

To determine molybdenum, evaporate the ether solution nearly to dryness by carefully heating over warm water, away from any flame. Add 10 ml of sulfuric acid and again evaporate to remove hydrochloric

* *J. Am. Chem. Soc.*, **30**, 1228.

acid. Cool, dilute with 100 ml of water and reduce the ferric salt by adding ammonium bisulfite. Boil off the excess of sulfurous acid, cool, transfer to a pressure-flask, saturate with hydrogen sulfide, and determine molybdenum as MoO_3 according to p. 274.

Take the aqueous-acid extract from the ether separation for the determination of vanadium. Remove the dissolved ether by heating on the water-bath, add nitric acid in excess and evaporate to remove hydrochloric acid. When the solution is almost sirupy, add 20 ml of hot water and heat with a few drops of sulfurous acid to reduce any chromic acid that may have been formed, but take care not to reduce the vanadium. Boil and slowly pour the hot solution, while stirring, into an excess of a boiling 10 per cent solution of sodium hydroxide. One milliliter of the alkali will neutralize about 0.4 ml of 6 N nitric acid. Boil a few minutes, allow the precipitate to settle, filter and wash with hot water till free from alkali. The precipitates contain hydroxides of iron, chromium, nickel, copper, manganese, etc., and the filtrate contains sodium vanadate. To remove traces of chromium, make acid with nitric acid, boil, and again neutralize with hot caustic soda. Make this last filtrate acid with acetic acid, heat to boiling, and precipitate the vanadium with hot lead acetate solution. Filter off the yellow lead vanadate precipitate, dissolve it in hot dilute hydrochloric acid and, if much lead is present, evaporate the solution nearly to dryness, cover with alcohol, and filter off the lead chloride. Evaporate off the alcohol and titrate the vanadium as in the preceding method.

Usually it is unnecessary to remove the lead. Evaporate the hydrochloric acid solution to dryness, add 50 ml of 12 N hydrochloric acid, and again evaporate nearly to dryness. Add 10 ml of concentrated sulfuric acid and evaporate to fumes. Cool, dilute to 150 ml, heat to 60° and titrate slowly with permanganate. One milliliter of 0.1 N permanganate reacts with 0.00510 g of vanadium.

Remark. — For the routine analysis of vanadium in steel, the American Society of Testing Materials has sanctioned the determination of vanadium without removing chromium. In this case, after the removal of the ether in the above procedure, add 25 ml of concentrated sulfuric acid and evaporate to fumes. Cool; add 25 ml of water and a slight excess of 2.5 per cent permanganate solution. Add 15 ml of concentrated hydrochloric acid, again evaporate to fumes, cool, dilute to 150 ml, and titrate with permanganate at 60°.

Campagne* showed that good results can be obtained by reducing the vanadium by evaporation with hydrochloric acid when not more than 0.1 g of vanadium is present. The reduction with sulfurous acid, as in the preceding method, is safer.

* *Compt. rend.*, **137**, 570 (1903).

METALS OF GROUP I

SILVER, LEAD, MERCUROUS MERCURY (AND THALLIUM)

The determination of lead and mercury has already been considered; it remains only to discuss the determination of silver.

SILVER, Ag. At. Wt. 107.88

Forms: AgCl and Ag

Determination as Silver Chloride, AgCl

Heat the solution, slightly acid with nitric acid, to boiling and precipitate the silver by the addition of hydrochloric acid, drop by drop, until no more precipitate is formed. Allow the precipitate to settle in a dark place, filter through a Gooch crucible, and wash, first with water containing a little nitric acid until the chloride test can no longer be obtained and then twice with alcohol or water to remove the nitric acid. Dry the precipitate at 100° and finally at 130° till a constant weight is obtained. If it is not desired to use a Gooch crucible for this determination, filter off the silver chloride upon an ordinary washed filter, wash as before and dry at 100°. Transfer as much of the precipitate as possible to a weighed porcelain crucible, burn the filter (as described on p. 32), and add the ash of the filter to the main portion of the precipitate. Moisten with a little nitric acid and a drop or two of concentrated hydrochloric acid, dry on the water-bath, and heat over a free flame until the silver chloride begins to melt. Weigh after cooling in a desiccator.

*Solubility of Silver Chloride.** — One liter of water dissolves 0.00154 g AgCl at 20° and 0.0217 g at 100°. In water containing a *little* hydrochloric acid, the AgCl is less soluble than in pure water, but as the quantity of hydrochloric acid is increased, the solubility of AgCl rises rapidly. Thus 1 l of 1 per cent HCl dissolves only 0.0002 g AgCl at 21°, but 1 l of 5 per cent HCl dissolves 0.0003 g, and 1 l of 10 per cent HCl dissolves 0.0555 g AgCl. By melting the silver chloride there is always loss by volatilization.

Determination as Metal, Ag

Metallic silver is obtained by the ignition of silver oxide, carbonate, cyanide, or the salt of an organic acid. In the latter case, the substance must be heated very cautiously at first in a covered crucible. When the organic substance is completely charred, remove the cover from the crucible and heat until the carbon is completely burned; then weigh the crucible.

* G. S. Whitby, *Z. anorg. Chem.*, **67**, 108 (1910).

From the chloride, bromide (but not the iodide), and sulfide, the metal can be obtained by igniting in a current of hydrogen. The reduction of the chloride, bromide, and iodide can be effected very conveniently by passing the electric current through the substance after it has been melted together. Place the porcelain crucible containing the silver halide in a crystallizing dish and near it place a second crucible containing a little mercury and a small piece of zinc. Upon the silver salt place a small disk of platinum foil, fastened to a platinum wire which dips into the mercury in the other crucible. Fill the crystallizing dish with 1.5 N sulfuric acid so that the crucible is entirely covered with the acid and allow to stand over night. Next morning all the silver salt will be found to be reduced. Remove the crucible from the acid, wash with water, dry, ignite, and weigh. By this simple method, E. Lagutt obtained excellent results. If the silver halide has not been fused to a compact mass, small particles of the silver precipitate are likely to float around during the operation, and escape reduction.

Separation of Silver from Other Metals

As almost all metal chlorides* are soluble in dilute hydrochloric acid, silver is usually separated from the other metals by the addition of hydrochloric acid to the solution. If the solution contains mercurous salts these are oxidized before the addition of the hydrochloric acid by boiling with nitric acid.

For the separation of silver from gold and platinum in alloys consult pp. 250, 255, and 261.

Electrolytic Determination of Silver

Silver may be deposited from nitric acid solutions, from ammoniacal solutions, and from potassium cyanide solution.

From nitric acid solution, the electrolysis succeeds under the following conditions: 0.5 g of silver in 150 ml of 0.1 N nitric acid electrolyzed at 55–60° with the voltage kept between 1.35 and 1.38 volts. Add 5 ml of alcohol to the bath to prevent the formation of peroxide at the anode. From 6 to 8 hours are required to precipitate the last traces of silver. Wash the electrode without interrupting the current, and dry at 100°.

* Thallous chloride is difficultly soluble in water. If thallium is present precipitate the silver from a nitrate solution by means of H_2S, ignite in a stream of hydrogen, and weigh as metal. To determine the thallium, evaporate the filtrate to dryness, dissolve the residue in a little water, and precipitate the thallium by the addition of potassium iodide. Wash the thallous iodide precipitate with dilute potassium iodide solution, then with alcohol, dry at 150°, and weigh as TlI.

Determination of Silver in Alloys with Baser Metals by Dry Assay

The cupellation of a silver alloy is carried out in much the same way as discussed under the Determination of Gold. Use 0.5 g of the alloy and first determine the approximate silver content by a trial assay. Cupel with 5 g of lead, and weigh the resulting button as described on p. 252. If the silver is 50 per cent or less, use 8 g of lead for the final assay. For each per cent of increase in silver content, use 0.1 g less of lead until the content corresponds to 80 per cent silver. Then decrease the weight of lead more rapidly with increase in the silver content, using 3.5 g of lead for a 90 per cent alloy, 2.3 g of lead for a 93.5 per cent alloy, 1.75 g of lead for a 95 per cent alloy, and only 0.6 g of lead for nearly pure silver. Unless care is taken to adjust the lead carefully to the silver content, the loss of silver during cupellation is likely to be serious.

For the final assay, cupel 0.5 g of the alloy with the suitable quantity of lead and weigh the button. Correct for loss of silver by volatilization and absorption by the cupel, by cupelling in the same way and at the same time the corresponding quantities of pure silver and copper. Without this correction, the results are usually 0.4–1.1 per cent too low.

GRAVIMETRIC DETERMINATION OF THE ACID CONSTITUENTS (ANIONS)

GROUP I

HYDROCHLORIC, HYDROBROMIC, HYDRIODIC, HYDROCYANIC, FERROCYANIC, FERRICYANIC, THIOCYANIC, AND HYPOCHLOROUS ACIDS

HYDROCHLORIC ACID, HCl. Mol. Wt. 36.46

Form: Silver Chloride, AgCl

A. The chlorine is present in solution either as free hydrochloric acid or as a chloride soluble in water.

B. It is present in the form of an insoluble chloride.

A. The Chloride is Present in Aqueous Solution

If only metals of the alkali or alkaline-earth groups are present, make the cold solution slightly acid with nitric acid, and slowly add silver nitrate with constant stirring until the precipitate coagulates and further addition of the reagent produces no more precipitation. Now heat the liquid to boiling, allow the precipitate to settle in the dark, filter through a Gooch crucible, and treat the AgCl precipitate exactly as described in the determination of silver, p. 297.

If the aqueous solution contains a chloride of a heavy metal, it is not always possible to follow the above procedure. If, for example, substances are present which on boiling are changed to insoluble basic salts, it is evident that the precipitate of silver chloride would be contaminated with these substances and too high results would be obtained. This is particularly true of stannic and ferric salts. Ferrous salts, on the other hand, if only little nitric acid is present, reduce silver nitrate to metallic silver on heating the solution; if enough nitric acid is present to prevent the reduction to silver, the danger of forming basic salts still remains. In such cases the precipitation is effected as before from a cold solution and the subsequent heating is omitted.

Invariably, however, it is better first to remove the heavy metal by precipitation with ammonia, caustic soda, or sodium carbonate.

Example: Analysis of Commercial Tin Chloride

Tin chloride is obtained either as a solid salt corresponding to the formula $SnCl_4 + 5\,H_2O$, or as a concentrated aqueous solution. As both the solid salt and its concentrated solution are very hygroscopic,

it is necessary to weigh out the portion for analysis from a stoppered vessel. It is best to proceed as follows:

Place a large sample of the substance (about 10 g) in a tared weighing beaker, stopper, and weigh. Dissolve in about 10 ml of water, shaking until a homogeneous sirup is obtained. Again weigh the beaker and its contents. Weigh 4 more weighing beakers, and in each place about 2 ml of the sirup. Quickly stopper each beaker and weigh.

Determination of Tin. — Wash the contents of one of the weighing beakers into a 400–500 ml beaker, dilute to about 300 ml, and add a few drops of methyl orange indicator solution, whereby the liquid is colored red. Add ammonium hydroxide solution (free from chloride) until the color of the solution is changed to yellow (an excess of ammonia must be carefully avoided for tin hydroxide is somewhat soluble in ammonia). To the neutral solution add 10 ml of $3\,N$ ammonium nitrate solution, boil 1 or 2 minutes, filter, wash with water containing ammonium nitrate, and weigh as SnO_2.

Determination of Chlorine. — Make the filtrate from the tin hydroxide precipitate acid with nitric acid, and precipitate in the cold with silver nitrate. Then heat the solution to boiling and, after the precipitate has settled, filter through a Gooch crucible, wash with cold water containing a little nitric acid, then with cold water or alcohol, dry at 130° C, and weigh.

The amount of tin and chlorine present is computed as follows: Let A = weight of the original solid salt, B = weight of the solid salt mixed with a little water; a = weight of the concentrated solution taken for analysis; p = weight of SnO_2 obtained; and q = weight of silver chloride.

Then $$\frac{\mathrm{Sn} \times p \times B \times 100}{\mathrm{SnO_2} \times a \times A} = \text{per cent Sn}$$

and $$\frac{\mathrm{Cl} \times q \times B \times 100}{\mathrm{AgCl} \times a \times A} = \text{per cent}$$

This analysis may be accomplished much more rapidly by a volumetric process. (Consult Volumetric Analysis.)

If antimony or stannous compounds are present, the above procedure cannot be used. It has been proposed to add tartaric acid to the solution, then dilute with water and precipitate the chlorine with silver nitrate. It is better, however, to proceed as follows: Precipitate the antimony by hydrogen sulfide, remove the excess of the latter by passing carbon dioxide through the solution, filter and wash the precipitate with hot water. Make the filtrate slightly ammoniacal, add a little hydrogen peroxide or potassium percarbonate (both reagents must be free from

chloride) and boil the solution until the excess of the peroxide is destroyed. By this treatment traces of hydrogen sulfide remaining in the solution are oxidized to sulfuric acid. After cooling, make acid with nitric acid, and determine the chlorine as described above.

According to this method, chlorine may be determined in the presence of large amounts of hydrogen sulfide without difficulty.

It is less practical to proceed as follows: Add an excess of ammonium hydroxide to the filtrate from the antimony sulfide and precipitate the excess hydrogen sulfide by adding ammoniacal silver nitrate solution. Filter off the deposited silver sulfide, wash with ammonia, and precipitate the silver chloride from the filtrate by acidifying with nitric acid and adding more silver nitrate if necessary.

B. Analysis of an Insoluble Chloride

Boil the substance with sodium carbonate solution* (free from chloride), and determine the chlorine in the filtrate as described above.

Some chlorides, *e.g.*, silver chloride, many minerals such as apatite,† sodalite, and rocks containing them are not decomposed by boiling with sodium carbonate. Such substances must be *fused* with sodium carbonate.

Mix silver chloride with three times as much sodium carbonate and heat in a porcelain crucible until the mass has sintered together. Extract with water, filter off the insoluble silver, and determine the chlorine in the filtrate as under (*a*).

For the determination of chlorine in rocks, fuse 1 g of the finely powdered material with four or five times as much sodium carbonate (or with a mixture of equal parts sodium and potassium carbonates) at first over a Bunsen burner, afterward over a Méker burner or the blast lamp. Extract the melt with hot water. After cooling, add methyl orange indicator solution, acidify with nitric acid, and allow to stand over night. If silicic acid has precipitated out by the next morning, add a little ammonia, boil the solution, filter, and wash with hot water. Add a little nitric acid to the cold filtrate and determine the chlorine as above.

If there is no separation of silicic acid on acidifying the water ex-

* Mercurous chloride is decomposed only slowly by sodium carbonate solution, but readily acted upon by potassium or sodium hydroxide.

† According to Jannasch, chlorine in apatite may be determined by treating the finely powdered mineral with nitric acid and silver nitrate on the water-bath. Everything goes into solution with the exception of silver chloride, which is filtered off and weighed. (This does not apply to a sample of apatite contaminated with silica or silicates.)

traction of the fusion with nitric acid,* precipitate the chlorine at once from the cold solution.

Free Chlorine

If it is desired to determine gravimetrically the amount of chlorine in a sample of chlorine water, it is not feasible simply to add silver nitrate, for not all the chlorine is precipitated as silver chloride; a part of it remains in solution as soluble chloric acid:

$$3\ Cl_2 + 3\ H_2O + 5\ AgNO_3 = 5\ \mathbf{AgCl} + HClO_3 + 5\ HNO_3$$

The chlorine, therefore, must be changed to hydrochloric acid or to one of its salts before attempting to precipitate with silver nitrate. This may be accomplished in several ways:

1. Transfer a definite amount of the chlorine water by means of a pipet to a flask containing ammonia water and after mixing heat the solution to boiling. After cooling, acidify with nitric acid and precipitate with silver nitrate. The ammonia converts the chlorine to ammonium chloride:

$$8\ NH_4OH + 3\ Cl_2 = 6\ NH_4Cl + N_2 + 8\ H_2O$$

2. Treat the chlorine water with an excess of sulfurous acid, make the solution ammoniacal, add hydrogen peroxide, and boil the liquid until the excess of hydrogen peroxide is removed. Cool, acidify with nitric acid, dilute with water, and precipitate the chlorine by means of silver nitrate.

3. Treat the chlorine water with dilute sodium hydroxide solution, and add an aqueous solution of sodium arsenite (arsenic trioxide dissolved in sodium carbonate) until a drop of the liquid will not turn a piece of iodo-starch paper blue. Then make acid with nitric acid and precipitate the chlorine by a soluble silver salt.

If the solution contains both free chlorine and hydrochloric acid determine the total chlorine by one of the above methods, and the free chlorine in a separate sample by a volumetric process (see Iodometry).

Determination of Chlorine in Non-electrolytes (Organic Compounds)

A. Method of Carius†

Principle. — The method is based upon the fact that all organic compounds are decomposed by heating with concentrated nitric acid at a high temperature under pressure. If the substance contains halogen, sulfur, phosphorus, or arsenic, it is

* According to W. F. Hillebrand, no separation of silicic acid is to be feared from 1 g of the substance.

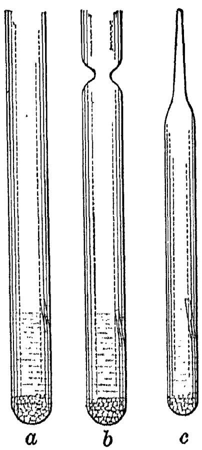
† *Ann. Chem. Pharm.*, **136**, 129 (1865) and *Z. anal. Chem.*, **4**, 451 (1865).

first set free as such, but on account of the reducing action of the nitrous acid formed it is then changed over into its hydrogen compound. The latter, however, is partly oxidized by the nitric acid. The reaction is therefore a reversible one. If, on the other hand, the substance is heated under the same conditions with nitric acid in the presence of silver nitrate, the halogen hydride is converted into silver halide as fast as it is formed and the halogen is in this case quantitatively changed into its silver salt. Sulfur, phosphorus, and arsenic are oxidized in the same way to sulfuric, phosphoric, and arsenic acids and any metals present form nitrates.

Procedure for the Halogen Determination

Take a tube made of difficultly fusible glass about 50 cm long, 2 cm in diameter, with walls about 2 mm thick. Seal one end, clean thoroughly, and dry by sucking air through it.

Transfer about 0.5 g of powdered silver nitrate (of substances rich in halogen as much as 1 g may be used) to the tube by pouring the powder through a cylinder made by rolling up a piece of glazed paper and shoving the paper into the tube until it reaches about the middle of it. Pour into the tube through a funnel whose stem is about 40 cm long, 2–5 ml of pure nitric acid (*d.* 1.5) free from chlorine. In this way only the lower half of the tube is wet with the acid. Incline the tube to one side and introduce a small glass tube, closed at one end and containing from 0.15 to 0.2 g of the substance (this smaller tube should be about 5 cm long and 5 mm wide). As soon as the tube containing the substance has reached the acid, it remains suspended (Fig. 62, *a*). It is very important that the substance should not come in contact with the acid before the tube is closed at the upper end, as otherwise there is likelihood of some halogen escaping.


a *b* *c*
FIG. 62.

Now heat the upper end of the tube very cautiously in the flame of the blast lamp until the tube begins to soften and thicken (Fig 62, *b*). Then draw out into a thick-walled capillary 3–5 cm long, and fuse the end together (Fig. 62, *c*).

After the tube has become cold, envelop it in asbestos paper, carefully shove it into the iron mantle of a "bomb furnace," and gradually heat. Aliphatic substances are usually decomposed by heating 4 hours at 150–200°; substances of the aromatic series usually require from 8–10 hours' heating at 250–300°, and for some substances an even longer heating at a higher temperature is necessary. The time and temperature must be found out for each substance by experiment. The de-

composition is complete when on cooling the contents of the tube neither crystals nor drops of oil are to be recognized.* Regulate the heating so that after 3 hours the temperature of about 200° is reached, after 3 hours more 250–270°, and finally after another 3 hours a temperature of about 300° is attained.† After the heating is finished, allow the tube to cool completely in the furnace, remove the iron mantle together with the tube, and by slightly inclining the mantle bring the capillary of the tube out into the open air. Usually a drop of liquid will be found in the point of the capillary. In order not to lose this, carefully heat the outer point with a free flame, and by this means drive back the liquid into the other part of the tube. Now heat the point of the capillary more strongly‡ until the glass softens, and a hole is blown in the soft glass as a result of the pressure within the tube. The gas escapes with a hissing sound. When the contents of the tube are at the atmospheric pressure, make a scratch upon it with a file just below the capillary, and touch this with a hot glass rod, whereby the tube usually breaks and the upper part can be removed. Then carefully pour out the contents of the tube into a fairly large beaker, without breaking the little tube into which the substance was weighed, and wash out the inner part of the tube as well as its capillary with water. Dilute the liquid in the beaker to about 300 ml and heat to boiling. After cooling, filter off the insoluble silver halide through a Gooch crucible and weigh after washing and drying at 130°.

If it is thought that the precipitate is contaminated by fragments of broken glass, as is often the case even with careful work, decant the clear liquid through a filter, wash the residue by decantation with very dilute nitric acid to the disappearance of the silver reaction, and dissolve the residue (except when it is silver iodide) in warm ammonia water. Filter the solution through the same filter, but collect the filtrate this time in a fresh beaker. After washing the filter with dilute ammonia, acidify the filtrate with nitric acid, heat to boiling, and after allowing the silver chloride or bromide to settle in the dark, filter through a Gooch crucible, dry at 130°, and weigh.

In the case of silver iodide, it cannot be dissolved in ammonia and

* Sometimes, with substances rich in sulfur, crystals of nitrosyl sulfuric acid are formed and adhere to the sides of the tube. They are easily distinguished from crystals of the undecomposed substance.

† Such a high pressure is often attained that the tube bursts as soon as it is heated very hot. In such cases heat to only 200°, allow to cool, open the capillary, and release the pressure. Then fuse together again and heat to the desired temperature.

‡ Before heating, the tube and the hand should be wrapped in a towel to avoid accidents.

in this way separated from splinters of glass. Therefore, filter off the precipitate, together with the glass, through an ordinary washed filter (not a Gooch crucible), wash with dilute nitric acid, then once with alcohol in order to remove the nitric acid, and dry at 100°. Transfer as much of the precipitate as possible to a watch glass, burn the filter, and drop the ash into a weighed porcelain crucible. Add a little dilute nitric acid (to change any reduced silver into the nitrate), evaporate off the liquid on the water-bath, add a few drops of water and a drop of pure hydriodic acid, and again evaporate the contents of the crucible to dryness. Now add the main part of the precipitate, heat until it begins to fuse, and weigh. Cover the mass in the crucible with pure dilute sulfuric acid, add a piece of chemically pure zinc, and allow the crucible to stand over night. After this time the silver iodide will be completely reduced to metallic silver. Remove the zinc, and wash the residue by decanting several times with water until the iodide reaction can no longer be detected. Warm the residue with dilute nitric acid upon the water-bath, in order to dissolve the silver, filter the solution through a small filter. Wash the filter with water and dry; ignite it in a crucible and weigh the residue (the glass). This second weight deducted from the former gives the amount of silver iodide present.

This method is also suitable for obtaining lead and mercury from organic compounds in a form which can be precipitated by hydrogen sulfide.

The method of Carius is by far the best for the determination of halogens in organic substances when only one of the halogens is present. If two or three of them are present at the same time, the " lime method " is to be preferred.

B. The Lime Method

Into a glass tube made of difficultly fusible glass (about 40 cm long, 1 cm wide, and closed at one end), introduce a layer of lime (free from chloride) from 5 to 6 cm long, then about 0.5 g of substance, and finally 5 cm more of lime. Mix the substance thoroughly with the lime by means of a copper wire wound into a spiral. Nearly fill the tube with lime, place on its side, and gently tap, so that a small canal is formed above the lime. Place the tube in a small combustion furnace (cf. Carbon) and heat. First heat the front end of the tube, free from substance, to a dull redness, then the back end, and afterwards light the other burners, one after another, until finally the whole tube is at a dull red heat. After cooling, transfer the contents of the tube to a large beaker and dissolve the lime in dilute nitric acid free from chlorine. Filter off the carbon, and precipitate the halogen with silver nitrate.

If the lime contains calcium sulfate, this is reduced to sulfide, so that some silver sulfide is likely to be precipitated with the silver halide. In this case treat the solution with hydrogen peroxide (free from halogen) before enough nitric acid has been added to make the solution acid, boil the liquid to remove the excess of the reagent, then acidify, filter, and precipitate with silver nitrate.* In the analysis of substances rich in nitrogen, it is possible that some soluble calcium cyanide will be formed. In this case care must be taken that the silver precipitate contains no silver cyanide (cf. Separation of Cyanogen from Chlorine-Bromine, and Iodine, p. 314).

C. The Sodium Peroxide Method

Heat 0.2–0.3 g of the substance with a mixture of 10 g of powdered potassium hydroxide and 5 g of sodium peroxide in a nickel or iron crucible. Heat first in the hot closet at 85°. After some time remove the crucible from the closet and heat over a small flame, gradually raising the temperature until the flux is melted. Cool, extract the melt with water, filter, and determine the halogen as silver salt after adding nitric acid.

Remark. — For an excellent volumetric method for determining chlorine see the Volhard method.

HYDROBROMIC ACID, HBr. Mol. Wt. 80.92

Form: Silver Bromide, AgBr

Hydrobromic acid is determined exactly the same as hydrochloric acid. This is also true of the determination of free bromine and of bromine in non-electrolytes.

HYDRIODIC ACID, HI. Mol. Wt. 127.93

Forms: Silver Iodide, AgI, and Palladous Iodide, PdI_2

(a) Determination as Silver Iodide

The determination of hydriodic acid is carried out in exactly the same way as the analysis of hydrochloric acid. If it is desired to filter the silver iodide through an ordinary washed filter instead of through a Gooch crucible, the procedure described on p. 297 is used, converting the reduced metal to iodide by dissolving in nitric acid and adding hy-

* W. Biltz (*Chem. Ztg.*, **1903**, Rep. 142) separates the halides from sulfide by treating the precipitated silver salts with an ammoniacal sodium thiosulfate solution, whereby the silver halide goes into solution, from which the silver is precipitated as silver sulfide, by adding ammonium sulfide, and determined as silver.

driodic acid. If there is no hydriodic acid at one's disposal, place the main portion of the precipitate in a weighed porcelain crucible and heat until it begins to melt and then weigh. Place the filter ash in another crucible, and treat with nitric and hydrochloric acids, whereby the silver and any unreduced iodide are changed to silver chloride. Weigh the silver chloride and add the equivalent amount of silver iodide to the weight of the main part of the precipitate.

(b) *Determination as Palladous Iodide*

This important method for the separation of iodine from bromine and chlorine is carried out as follows:

Make the solution acid with hydrochloric acid, and add palladous chloride solution until no more precipitate is formed. After standing one or two days in a warm place, filter off the brownish black precipitate of palladous iodide through a Gooch crucible, or through a tared filter that has been dried at 100°, wash with warm water, dry at 100°, and weigh as PdI_2.

According to Rose, the PdI_2 may be changed to palladium by igniting in a current of hydrogen, and from the weight of the palladium the amount of iodine calculated.

SEPARATION OF THE HALOGENS FROM ONE ANOTHER

1. Separation of Iodine from Chlorine

(a) *The Palladous Iodide Method*

Determine the iodine as palladous iodide, and in a second sample determine the sum of the chlorine and iodine from the weight of their insoluble silver salts.

(b) *Method of Gooch*

This method depends upon the fact that, in a dilute acid solution of the three halides, nitrous acid reacts only with the iodide:

$$2\,KI + 2\,KNO_2 + 4\,H_2SO_4 = 4\,KHSO_4 + 2\,NO + 2\,H_2O + I_2$$

Iodine is liberated and escapes from the solution on boiling. In one sample, therefore, precipitate the halogens together in the form of their silver salts, in a second sample determine the amount of the chlorine after setting free the iodine by means of nitrous acid, and determine the amount of iodine by difference. In order to obtain correct results by this method, the solution must be very dilute when it is boiled to expel the iodine; otherwise some chlorine escapes.

Procedure. — Dissolve 0.5 g of the halide mixture in 600 ml of water in a liter flask, treat with 2–3 ml of dilute sulfuric acid, add 0.5–1 g of solid potassium nitrite (free from halogen), and boil the solution until

entirely colorless; usually this is accomplished in about three-quarters of an hour. Then add silver nitrate solution, and allow the resulting precipitate to settle. Filter through a Gooch crucible, and weigh.

(c) *Method of Jannasch**

Jannasch proceeds in exactly the same way as Gooch, but instead of letting the iodine escape, he collects in it an aqueous solution of sodium hydroxide and hydrogen peroxide, whereby it is transformed to sodium iodide and can be subsequently determined as silver iodide. In the other solution the chlorine is determined in the usual way.

Procedure. — Place the solution containing 0.5 g of the two halides in a $1\frac{1}{2}$-l round-bottomed flask and dilute to a volume of 600–700 ml. Like a wash-bottle, provide this flask with one glass tube reaching to the bottom, through which vapor can be conducted into the flask, and with another shorter tube for the escape of gas. Connect this second tube with an Erlenmeyer flask for a receiver, and this in turn with a Péligot tube. Place about 50 ml of pure 5 per cent sodium hydroxide solution in the Erlenmeyer flask, add an equal volume of hydrogen peroxide free from chlorine, and cool the mixture by surrounding the flask with ice or snow. Likewise fill the Péligot tube with a suitable amount of caustic soda and hydrogen peroxide. Now add from 5 to 10 ml of 6 N sulfuric acid and 10 ml of 10 per cent sodium nitrite solution to the solution containing the halides. Immediately close the flask, and heat the contents over a free flame while at the same time conducting steam into it. As soon as the liquid begins to boil, the space above is filled with violet vapors of iodine, which are gradually driven over into the Erlenmeyer flask, where, with evolution of oxygen, they are completely absorbed by the hydrogen peroxide solution. The iodine is changed into sodium iodide and sodium hypoiodite by means of the dilute alkali:

$$I_2 + 2\,NaOH = NaI + NaIO + H_2O$$

The sodium hypoiodite, however, is reduced by the hydrogen peroxide to sodium iodide:

$$NaIO + H_2O_2 = H_2O + O_2 + NaI$$

When all the iodine is driven over into the receiver (which is always the case after the solution in the flask has become colorless and has been boiled for 20 minutes longer), remove the delivery-tube between the distilling-flask and the Erlenmeyer flask, wash the liquid within with hot water into the Erlenmeyer, and stop the current of steam. Add the contents of the Péligot tube to the Erlenmeyer flask and heat

* *Z. anorg. Chem.* I, 144, and *Prakt. Leit. der Gewichtsanalyse.*

the solution to boiling to remove the excess of hydrogen peroxide. After cooling, make the liquid acid with a little sulfuric acid; this always causes a yellow coloration due to free iodine.* Treat the solution, therefore, with a few drops of sulfurous acid, to decolorize it. Add an excess of silver nitrate and a little nitric acid, boil the liquid, and filter the silver iodide into a Gooch crucible. Dry at 130° and weigh.

For the chlorine determination, transfer the contents of the distilling-flask to a beaker and determine the chlorine as silver chloride.

Determination of the Halogens by Indirect Analysis

2. Determination of Bromine together with Chlorine

Principle. — In this method the sum of the weights of the silver salts of the two halogens is first determined and afterwards the silver bromide is converted to silver chloride by heating in a current of chlorine.

Procedure. — To the neutral solution containing about 0.5 g of halides add a little nitric acid (free from chlorine) and precipitate in the cold by the addition of a slight excess of silver nitrate. Heat the liquid to boiling, with frequent stirring, cool after the precipitate has coagulated, and filter off the precipitate into a 15-cm long-asbestos filter tube made of difficultly fusible glass. Dry the precipitate at 150° and weigh after cooling.

For the transformation of the bromide into chloride, shove the asbestos forward a little in the tube by means of a glass rod (in order that the gas may pass through it more readily), fasten the tube in a slightly inclined position, and pass a current of dry chlorine gas through it. At the same time cautiously heat the tube by moving a small flame back and forth. During the first half hour the precipitate should not be heated hot enough to melt it; finally, however, raise the temperature until it *begins* to melt, after which replace the chlorine by air, cool, and again weigh.

If p represents the weight of silver chloride and bromide first obtained, q the weight after the precipitate has been completely changed to chloride, x the weight of silver chloride in the first precipitate, and y the weight of silver bromide, then $x + y = p$ and $x + \frac{AgCl}{AgBr} y = q$.

* If the above directions are closely followed, there should not be much separation of iodine. It may be caused by the presence of a small amount of nitrous acid which is not oxidized to nitric acid by hydrogen peroxide; or, if the contents of the Erlenmeyer flask are not kept cool, appreciable amounts of sodium iodate ($NaIO_3$) are formed, and the latter is not reduced by hydrogen peroxide. In this case there is a separation of a considerable amount of iodine on acidifying the solution, but the addition of sulfurous acid changes it to iodide without loss.

Since $\frac{\text{AgCl}}{\text{AgBr}} = 0.7633$, the solution of the above two equations gives $y = 4.224\ (p - q)$ and $x = p - y$, from which the percentage of chlorine and bromine can be computed.

3. Determination of Iodine together with Chlorine

The same procedure is used as above described.

If p represents the weight of silver iodide + silver chloride, q the weight after the silver has been converted to chloride, x the weight of silver chloride, and y the weight of silver bromide in the first precipitate, $y = 2.567\ (p - q)$ and $x = p - y$.

4. Determination of Bromine in the Presence of Iodine

In this case p represents the weight of the silver bromide and silver iodide, q as before the corresponding weight of silver chloride, x the weight of silver iodide in the first precipitate, and y the weight of silver bromide,

$$x + y = p, \qquad \frac{\text{AgCl}}{\text{AgI}}x + \frac{\text{AgCl}}{\text{AgBr}}y = q$$

$$x = 4.996\,p - 6.545\,q$$

$$y = p - x$$

5. Determination of Iodine, Bromine, and Chlorine

In one portion of the substance determine the weight p of silver salts obtained by precipitation and change this over to silver chloride of weight q. In another portion of the same weight of original substance, determine the weight t of palladous iodide corresponding to the iodine content. Then if x represents the weight of silver chloride and y the weight of silver bromide in the first precipitate, the following relationships hold:

$1.303\ t$ = weight of silver iodide in the first silver precipitate and $0.7951\,t$ is the corresponding weight of silver chloride.

$p - 1.303\,t$ = weight of silver bromide and silver chloride in the first precipitate.

$q - 0.7951\,t$ = weight of silver chloride in the second precipitate equivalent to the chloride and bromide.

$$x + y = p - 1.303\,t \qquad x + 0.7633\,y = q - 0.7951\,t$$

$$y = 4.224\,[(p - 1.303\,t) - (q - 0.7951\,t)]$$

$$x = p - 1.303\,t - y$$

Instead of determining the iodine as palladous iodide it may be removed as on p. 308, *b*, by treatment with nitrous acid and the weight of the silver bromide + silver chloride obtained.

Another method* depends upon the fact that treatment of silver halides with potassium dichromate and concentrated sulfuric acid causes the following decompositions:

$$6\,AgCl + K_2Cr_2O_7 + 14\,H_2SO_4 = 6\,AgHSO_4 + 2\,KHSO_4 + 2\,Cr(HSO_4)_3 + 7\,H_2O + 3\,Cl_2\uparrow$$

$$6\,AgBr + K_2Cr_2O_7 + 14\,H_2SO_4 = 6\,AgHSO_4 + 2\,KHSO_4 + 2\,Cr(HSO_4)_3 + 7\,H_2O + 3\,Br_2\uparrow$$

$$2\,AgI + 2\,K_2Cr_2O_7 + 18\,H_2SO_4 = 2\,AgHSO_4 + 4\,KHSO_4 + 4\,Cr(HSO_4)_3 + 8\,H_2O + 2\,HIO_3$$

All the bromine and chlorine can be distilled off, but the silver and all the iodine remain behind. By introducing SO_2 into the diluted acid, the iodic acid is reduced to hydriodic acid and silver iodide precipitates. After filtering this off, the remaining silver can be precipitated as iodide. Thus for the determination of the three unknowns, three simultaneous equations can be formulated.

Procedure. — Precipitate a mixture of silver chloride, bromide, and iodide in the usual manner, filter into a small asbestos filtering tube, and weigh after drying at 150°. Call the weight of original substance *A* and that of the mixed halides *a*. Place the dry precipitate together with the asbestos in an Erlenmeyer flask and for each 0.3 g of silver salt add 2 g of pure, potassium dichromate and 30 ml of concentrated sulfuric acid. Heat 2 hours at 95°. Toward the last, pass a stream of air through the liquid until all the chlorine and bromine has been expelled. The decomposition takes place more rapidly if the precipitate is treated with the oxidizing mixture without drying it except by suction, but this necessitates the determination of the mixed silver salts in a separate sample. After the oxidation of the silver salts is complete, dilute with 300 ml of water, filter off the asbestos, and to the filtrate add sodium bisulfite solution drop by drop until a faint permanent odor of sulfur dioxide is obtained. Filter off and weigh the silver iodide precipitate; call this weight *b*. In the filtrate precipitate the rest of the silver by adding potassium iodide. Call this weight *c*. Compute the percentages of chlorine, bromine, and iodine as follows:

$$\frac{54.06\,b}{A} = \text{per cent iodine}$$

* Bech, *Chem. Ztg.*, **39**, 405 (1915), Baubigny, *Compt. rend.*, **127**, 1219 (1898).

$$\frac{63.8\,c - 80.0\,(a - b)}{A} = \text{per cent chlorine}$$

$$\frac{179.8\,(a - b) - 109.7\,c}{A} = \text{per cent bromine}$$

Hydrocyanic Acid, HCN. Mol. Wt. 27.02

Forms: Silver Cyanide, AgCN, and Metallic Silver, Ag

Free hydrocyanic acid as well as the cyanides of the alkalies and alkaline earths are decomposed quantitatively by silver nitrate with the formation of insoluble silver cyanide.

If, therefore, it is desired to determine gravimetrically the amount of cyanide present in an aqueous solution of hydrocyanic acid or of an alkali cyanide, treat the cold solution with an excess of silver nitrate, stir, make faintly acid with nitric acid, allow the precipitate to settle and filter through a weighed filter, dry at 110°, and weigh. To confirm the result, place the silver cyanide in a porcelain crucible, burn the filter in a platinum spiral, add its ash to the main portion of the precipitate, and ignite the contents of the crucible, at first gently and finally more strongly but not enough to melt the silver. Cool and weigh the silver.

By the decomposition of the silver cyanide, difficultly volatile paracyanide is formed, but this is gradually burned away by igniting the contents of the open crucible.

Example: Determination of Hydrocyanic acid in Bitter-almond Water. — Bitter-almond water contains cyanogen as free hydrocyanic acid and as ammonium cyanide, but the greater part is present as mandelic acid nitrile, $C_6H_5CH(OH)CN$, which is not decomposed in aqueous solution by means of silver nitrate, but is readily acted upon by it if the solution is made ammoniacal after the addition of the silver nitrate and then made acid.

The gravimetric determination of the cyanogen present is performed according to the method of Feldhaus* as follows:

Treat 100 g of bitter-almond water with 10 ml of a 10 per cent silver nitrate solution, add 2–3 ml of concentrated ammonium hydroxide and immediately acidify with nitric acid. Allow the precipitate to settle, and determine the HCN as described above.

Liebig's volumetric method is much more satisfactory for this determination (see Part II, Precipitation Analyses).

If it is desired to determine the amount of cyanogen in a solid alkali cyanide, dissolve a weighed amount of the salt in water containing silver

* *Z. anal. Chem.*, **3**, 34 (1864).

nitrate, and make the solution acid with nitric acid and treat the precipitate as above.

If the cyanide is dissolved in water before the addition of the silver nitrate, there is always a slight loss of hydrocyanic acid.

Some complex cyanides are quantitatively decomposed by silver nitrate, *e.g.*, those of nickel, zinc, and copper (the last only slowly); others such as the ferro- and ferricyanides of the alkalies (and mercuric cyanide) are not.

Determination of Cyanogen in Mercuric Cyanide, Method of Rose

Mercuric cyanide is a non-electrolyte and is consequently not precipitated by silver nitrate, but it is acted upon by hydrogen sulfide with the formation of insoluble mercuric sulfide and hydrocyanic acid:

$$Hg(CN)_2 + H_2S = HgS + 2\,HCN$$

This reaction, however, cannot take place in neutral or acid solutions on account of the volatility of the hydrocyanic acid; it must be performed in an alkaline solution. In order to avoid the introduction of an excess of hydrogen sulfide into the solution, the following procedure is necessary:

Treat the aqueous solution of the mercuric cyanide with about twice as much zinc sulfate dissolved in ammonia. If this should cause a turbidity, add enough ammonia to clear it up and slowly add hydrogen sulfide water. This causes at first a brown precipitate which becomes black on stirring. Continue the addition of hydrogen sulfide water until the upper liquid shows a *pure white* precipitate of zinc sulfide. The zinc sulfate, therefore, serves, as it were, as an indicator, inasmuch as the pure white precipitate will not be formed until the mercury is completely precipitated. Filter off the precipitated sulfides and wash with dilute ammonia. The filtrate contains all the hydrocyanic acid. Add to it an excess of silver nitrate, make acid with nitric acid, filter, and determine the weight of silver in the silver cyanide as described on p. 313.

Determination of Hydrocyanic Acid and Halogen Hydride in the Presence of One Another, according to Neubauer and Kerner*

Treat the solution with silver nitrate in the cold, add nitric acid to faintly acid reaction, and heat to coagulate the precipitate. Filter, dry at 130°, and in this way determine the total weight of the silver salts. Place a definite amount of the precipitate in a porcelain crucible,

* *Ann. Chem. Pharm.*, **101**, 344 (1857).

heat until it is completely melted, and reduce with zinc and sulfuric acid as described on p. 306. Dilute with water, filter off the metallic silver and para-cyanogen, and determine the halogen in the filtrate according to pp. 300 *et seq.*

The above separation can be more satisfactorily effected by means of a volumetric process (see Precipitation Analyses).

Thiocyanic Acid, HCNS. Mol. Wt. 59.08

Forms: $Cu_2(CNS)_2$, AgCNS, $BaSO_4$

1. Determination as Cuprous Thiocyanate, $Cu_2(CNS)_2$

To the solution of thiocyanate, which is neutral or slightly acid with hydrochloric or sulfuric acid, add 20–50 ml of a saturated solution of sulfurous acid, and copper sulfate solution with constant stirring until a slightly greenish tint is imparted to the liquid. After standing a few hours, filter the precipitate into a Munroe crucible, wash with cold water containing sulfurous acid, then once with alcohol, and dry at 130° to constant weight.

2. Determination as Silver Thiocyanate, AgCNS

This excellent method for estimating thiocyanic acid is applicable only in the absence of the halogen acids or hydrocyanic acid.

Treat the dilute solution of the alkali thiocyanate in the cold with a slight excess of silver nitrate solution, which has been acidified with nitric acid. After stirring well, filter off the precipitate into a Munroe crucible, wash with water, then with a little alcohol, dry at 130°, and weigh.

3. Determination as Barium Sulfate

In the absence of all other compounds containing sulfur, thiocyanic acid can be determined with accuracy by oxidizing it and precipitating the sulfuric acid formed as barium sulfate. Bromine water is the most suitable oxidizing agent for this purpose. Treat the alkali thiocyanate solution with an excess of bromine water, heat for 30–60 minutes on the water-bath, acidify the solution with hydrochloric acid, precipitate the sulfuric acid by means of barium chloride, and weigh as barium sulfate (see Sulfuric Acid).

Determination of Thiocyanic and Hydrocyanic Acids in the Presence of One Another (Borchers)*

In one portion determine by volumetric titration the quantity of silver nitrate necessary to precipitate both of the acids (see Precipitation Analysis), and in a second portion determine the weight of barium sulfate formed after the oxidation of the thiocyanic acid. From the latter weight compute the quantity of thiocyanic acid present and also the weight of silver nitrate that would be required to precipitate it. If this weight is subtracted from the weight of silver nitrate required to precipitate both of the acids, the quantity of silver nitrate equivalent to the hydrocyanic acid present is obtained.

Determination of Thiocyanic Acid together with Halogen Hydrides (Volhard)

In one portion determine the thiocyanic acid as barium sulfate after oxidation. Heat a second portion in a closed tube with concentrated nitric acid and silver nitrate (Carius Method,† p. 303), filter off and weigh the mixture of silver halides and change to silver chloride as described on p. 310. Fuse a third portion with sodium carbonate and potassium nitrate, dissolve the alkali salts in water, and determine the iodine as palladous iodide (see p. 308). From the data thus obtained, compute the relative quantities of the three halides (see p. 310).

FERROCYANIC ACID, $H_4Fe(CN)_6$. Mol. Wt. 215.9

Form: Silver Cyanide, AgCN

The most accurate procedure for the analysis of complex cyanides is to determine the carbon and nitrogen by elementary analysis (which see).

Determination as Silver Cyanide (Rose-Finkener)

This method depends upon the fact that all salts of ferrocyanic acid on being heated with yellow mercuric oxide give up their cyanogen to the mercury, forming soluble mercuric cyanide, while the iron is changed to insoluble ferric hydroxide. Thus Prussian blue is decomposed as follows:

$$Fe_4[Fe(CN)_6]_3 + 9\,HgO + 9\,H_2O = 9\,Hg(CN)_2 + 4\,Fe(OH)_3 + 3\,Fe(OH)_2$$

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* *Repertorium der anal. Chemie*, 1881, p. 130.

† Instead of using the Carius method, the halogens and thiocyanate may be precipitated by silver nitrate, filtered through a Gooch crucible, dried at 160°, and weighed.

Treat a weighed amount of the substance with water and an excess of mercuric oxide. Boil until the blue color has completely disappeared, filter off the iron precipitate with the excess of mercuric oxide, and determine the cyanide in the filtrate according to p. 314.

On filtering off the insoluble oxides, at first a clear filtrate is obtained, but on washing some of the precipitate usually passes through the filter. By washing with a solution containing a dissolved salt, preferably mercuric nitrate, it is possible, however, to obtain a clear filtrate. Even then the operation is tedious, so that it is better to dilute the liquid containing the precipitate suspended in it to 100 ml, and use a filtered aliquot of 50 ml for the determination of the cyanide according to p. 314. A slight error is introduced because the volume of the precipitate is neglected, but it is largely compensated by adsorption errors.

Soluble ferrocyanides may be determined satisfactorily by titration with potassium permanganate (cf. Part II, Oxidation and Reduction Methods). For the determination of the iron and other metals, heat the substance with concentrated sulfuric acid, dissolve the residue after evaporation in water, and analyze the solution in the usual way.

FERRICYANIC ACID, $H_3Fe(CN)_6$. Mol. Wt. 214.9

The ferricyanides are analyzed in the same way as the ferrocyanides.

HYPOCHLOROUS ACID, HClO. Mol. Wt. 52.47

Hypochlorous acid is always determined volumetrically and will be discussed in Part II of this book, under Oxidation Methods.

GROUP II

NITROUS, HYDROSULFURIC, ACETIC, CYANIC, AND HYPOPHOSPHOROUS ACIDS

NITROUS ACID, HNO_2. Mol. Wt. 47.02

Nitrous acid is determined either volumetrically, gasometrically, or colorimetrically. The first two methods will be discussed in Parts II and III of the book.

Colorimetric Determination, of Peter Griess

This method serves only for the determination of extremely small amounts of nitrous acid (*e.g.*, in drinking-waters), and depends upon the formation of intensively colored azo-dyes.

Inasmuch as azo-compounds are formed only when nitrous acid is

present, they can all be used in testing for this acid, but the different substances do not prove equally sensitive as reagents. Thus in the production of tri-amino-azo-benzene (Bismarck brown) not less than 0.02 mg of nitrous acid in a liter can be detected, whereas according to the following procedure 0.001 mg in a liter can be detected with certainty. To carry out the determination two solutions are necessary, one of sulfanilic acid and one of α-naphthylamine. Both substances are dissolved in acetic acid* and prepared according to the directions of Ilosvay† as follows:

1. Dissolve 0.5 g of sulfanilic acid in 150 ml of dilute acetic acid.

2. Boil 0.1 g of solid α-naphthylamine with 20 ml of water, pour off the colorless solution from the bluish violet residue, and add 150 ml of dilute acetic acid.

Mix these two solutions.‡ It is not necessary to protect the reagent from the action of light, but it is desirable to keep impure air away from it. As long as the solution remains colorless it can be used. If it comes in contact with nitrous acid, which is often present in the air, the reagent becomes red and must be decolorized by shaking with zinc-dust before using.

Besides the above reagent, it is necessary to prepare a solution of sodium nitrite of known strength. For this purpose add silver nitrate solution to a concentrated solution of commercial potassium nitrite, filter off the precipitated silver nitrite, and wash a few times with cold water. To obtain absolutely pure silver nitrite dissolve the precipitate in as little hot water as possible and quickly cool. Place the mass of crystals in a funnel provided with a platinum cone and, after draining off the mother-liquor by suction, wash with a small amount of distilled water. Place the silver nitrite in a calcium chloride desiccator and allow to dry in the dark. As soon as it has become dry (shown by its having assumed a constant weight) dissolve exactly 0.4047 g in a liter flask with hot distilled water. Add 0.2–0.3 g of pure sodium chloride (*i.e.*, a little more than the theoretical amount) to convert the silver nitrite into silver chloride and sodium nitrite. Cool, dilute the solution to exactly 1 l with pure water, shake well, and allow the precipitate to settle. After this, pipet off 100 ml of the clear liquid into a second liter flask and dilute up to the mark with water free from nitrous acid. One milliliter of this solution contains 0.01 mg N_2O_3.

* P. Griess used dilute sulfuric acid to set free the nitrous acid. Ilosvay showed that if acetic acid were used the reaction was much more sensitive.

† *Bull. chim.* [2] **2**, 317.

‡ Lunge, *Zeitschr. f. angew. Chem.*, 1899, Heft 23.

Procedure for the Determination

Place 50 ml of the water to be examined in a cylinder, such as is shown on p. 77, add 5 ml of the reagent, and mix the contents of the cylinder with the aid of the stirrer shown in Fig. 32, p. 77. Place the cylinder in water heated to 70–80°. If as much as 0.001 mg of nitrous acid is present in a liter of the water tested, the red coloration will appear within 1 minute; with relatively larger amounts (*e.g.*, as much as 1 mg per liter) the solution is simply colored yellow, unless a concentrated solution of naphthylamine is used. Meanwhile in three other cylinders place respectively 0.1 ml, 0.5 ml, and 1 ml of the solution containing a known amount of sodium nitrite; dilute each with water up to the mark and treat with the reagent in the same way. As soon as a distinct red coloration is apparent, compare the colors with that produced by the water to be analyzed. If the color of the unknown water lies between two of the standards — *e.g.*, between that produced with 0.1 and 0.5 ml of the standard — then prepare 3 more standards containing, say, 0.2, 0.3, and 0.4 ml of the known solution. When the color of the unknown solution is matched, then the water contains the same amount of nitrous acid as the standard.

If the water contains considerable nitrous acid (*e.g.*, over 0.3 mg per liter), the red coloration will be so dark that the colorimetric determination cannot be performed with certainty. In this case dilute a definite volume of the water with distilled water and determine the nitrous acid present in this diluted water.

Tromsdorff recommends for the determination of nitrous acid in drinking-water the use of zinc iodide of starch, and comparing the blue color produced by the nitrous acid (cf. Vol. I). If 0.1 mg of nitrous acid is present in a liter, the blue color produced can be distinctly seen; with 0.4 mg per liter, however, the color is so intense that it is unsuited for a colorimetric determination. This method is not to be recommended because in the first place it is far less sensitive than the Griess method, and second because it can easily lead to error inasmuch as a blue color will be often produced when there is no nitrous acid present. Traces of hydrogen peroxide or ferric salts, which are likely to be present in a drinking-water, will also cause the solution of zinc iodide of starch to turn blue.

HYDROGEN SULFIDE (HYDROSULFURIC ACID), H_2S. Mol. Wt. 34.08

Forms: Barium Sulfate, $BaSO_4$, Hydrogen Sulfide, H_2S, and colorimetrically

There are four cases to be considered:

I. The determination of free hydrogen sulfide.

II. The determination of sulfur in sulfides soluble in water.

III. The determination of sulfur in sulfides insoluble in water but decomposable by dilute acids with evolution of hydrogen sulfide.

IV. The determination of sulfur in insoluble sulfides.

I. Determination of Free Hydrogen Sulfide

(a) Determination of Hydrogen Sulfide in Gas Mixtures

If it is desired to know the percentage of hydrogen sulfide present in a mixture of gases, the analysis is best made volumetrically (see Part II, Iodometry), but it is possible to accomplish the same end by a gravimetric process.

Connect the source of the gas by means of rubber tubing with a ten-bulb Meyer absorption tube,* which contains a solution of ammoniacal hydrogen peroxide free from sulfuric acid. Connect the other end of the absorption tube with an aspirator, *i.e.*, a large bottle of about 4–5 liters capacity filled with water and closed by means of a double-bored stopper. Through one hole of the stopper pass a right-angled glass tube which reaches just below the bottom of the stopper in the bottle, and connected at other end with the absorption tube. Through the other hole in the stopper place a glass tube reaching to the bottom of the bottle. Likewise bend the upper end of this tube, and connect with a rubber tube to serve as a siphon; on the lower end of the rubber tube place a screw-cock.

Before beginning the experiment, remove the air in the rubber tubing between the source of gas and the absorption tube by conducting the gas to be analyzed through it. When this is accomplished connect the tubing with the absorption tube. Now allow water to run slowly from the aspirator into a vessel graduated in liters; after from 2 to 5 liters of the water have run out, close the aspirator by screwing up the cock on the siphon arm. Pour the contents of the absorption tube into a beaker, slowly heat to boiling, and keep at this temperature for 5–10 minutes. Evaporate the solution on the water-bath to a small volume, add a little hydrochloric acid, filter the solution if necessary, and precipi-

* Generally two of these tubes are used in order to make sure that none of the gas escapes absorption.

tate the sulfuric acid at a boiling temperature with a boiling solution of barium chloride. After the precipitate has settled, filter it off, ignite wet in a platinum crucible, and weigh as barium sulfate.

Both at the beginning and end of the experiment it is necessary to note the temperature of the room and the barometer reading. Use the mean of these readings for the calculation. Compute the amount of hydrogen sulfide present in the gas as follows:

The volume of water which has flowed out of the aspirator represents the volume of the gas that has been sucked through the apparatus less the amount absorbed by the ammoniacal hydrogen peroxide solution. Let V represent the volume of water in liters which has flown from the aspirator and p the weight of barium sulfate found.

Since one gram molecule of barium sulfate corresponds to one gram molecule of hydrogen sulfide and the latter assumes at 0° and 760 mm pressure a volume of 22.16 liters,* we have:

$$V_1 = \frac{22.16 \cdot p}{BaSO_4} = \text{the volume of the hydrogen sulfide absorbed.}$$

Now the volume (V) of the gas that passed through the apparatus was at $t°$ and B millimeters pressure and was saturated with water vapor; whereas V_1 refers to the dry gas at 0° C and 760 mm pressure. It is necessary, therefore, to reduce V to 0° C and 760 mm pressure.

$$V_0 = \frac{V \cdot (B - w)\, 273}{760\,(273 + t)}$$

The volume of the gas drawn through the apparatus is then:

$$V_0 + V_1$$

and we have: $\frac{V_1 \cdot 100}{V_0 + V_1}$ = the percentage by volume of hydrogen sulfide present.

(b) *Determination of Hydrogen Sulfide Present in Solution*

By means of a pipet measure out a definite volume of the solution and allow it to run into ammoniacal hydrogen peroxide while constantly stirring with the pipet. Heat to boiling, acidify with hydrochloric acid, and determine the amount of sulfate by precipitation with barium chloride.

II. Determination of Sulfur in Sulfides Soluble in Water

(α) Treat the solution with an excess of ammoniacal hydrogen peroxide water, slowly heat to boiling and keep at this temperature

* According to Leduc, *Comp. rend.*, **125**, 571 (1897) the density of H_2S (referred to air = 1) is 1.1895, from which the molecular volume is computed as 22.159 liters.

until the excess of the reagent is destroyed. Then precipitate the sulfuric acid with barium chloride and weigh as barium sulfate.

(β) Treat the solution with bromine water until a permanent brown color is obtained, heat, make acid with hydrochloric acid, and determine the sulfuric acid as barium sulfate.

If the solution contains thiosulfate, sulfide, and sulfate, as it is likely to after standing in the air for some time, precipitate the sulfide sulfur by means of cadmium acetate and determine the sulfur in the precipitate as under III, or oxidize the cadmium sulfide with either bromine water or fuming nitric acid, and determine the sulfuric acid formed as barium sulfate.

The determination of thiosulfate, sulfide, and sulfite sulfur will be discussed in Part II of this book under Iodometry.

III. The Determination of Sulfur in Sulfides Soluble in Dilute Acids

Principle. — The hydrogen sulfide is evolved by treatment of the sulfide with dilute acid, and absorbed in ammoniacal hydrogen peroxide solution as under I; or the hydrogen sulfide is absorbed in caustic soda solution and the sodium sulfide formed analyzed according to II; or finally the gas may be absorbed in a weighed tube containing pumice soaked with copper sulfate solution, the gain in weight representing the amount of gas absorbed.

Evolution and Absorption of the Hydrogen Sulfide

Of sulfides rich in sulfur take 0.25–0.50 g of the substance for analysis, and of sulfides containing less sulfur use a correspondingly larger amount. Place the substance in an Erlenmeyer flask (Fig. 63, *a*), break the connection between the flask and the receiver, and expel the air from *K* by conducting hydrogen gas through the delivery tube and out through the open stopcock of *T*. After a rapid current of hydrogen has passed through the apparatus for about 5 minutes, partly fill the receivers *V* and *P* with an ammoniacal solution of hydrogen peroxide* (about 3–4 per cent H_2O_2), place about 100 ml of the solution in *V* and about 10–20 ml in *P*.

Now connect the receiver, *V*, with the delivery tube from the evolution flask *K*, and conduct hydrogen from *T* through the whole apparatus for 5 minutes more in order to remove as much as possible of the

* Instead of hydrogen peroxide, the receivers can contain 100 ml of dilute sodium hydroxide solution (250 g to 1 l). After the decomposition is complete transfer the contents of the receiver to a beaker, add 30–50 ml of bromine water, make the solution acid with hydrochloric acid, and boil while passing carbon dioxide through it until the excess of bromine is completely expelled. Then precipitate the sulfuric acid formed with a hot solution of barium chloride. Instead of oxidizing the sodium sulfide to sodium sulfate it can be titrated with iodine (cf. Iodometry).

air from the receivers. After this, introduce about 20 ml of boiled water into K through T so that the substance is entirely covered, then slowly add $6N$ hydrochloric acid to the contents of the flask and promote the decomposition by warming somewhat. When the evolution of the gas has ceased, heat the contents of K to gentle boiling and pass a slow current of hydrogen* through the apparatus from T for 20 minutes; then remove the flame and continue the current of hydrogen for 15 minutes longer. At the end of this time, the hydrogen sulfide will be completely driven over into V.†

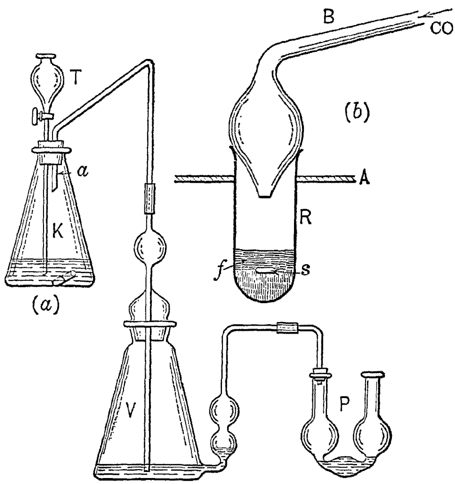

Fig. 63.

Wash the contents of the two receivers into a beaker and slowly heat to boiling in order to effect the complete oxidation of the thiosulfuric and sulfurous acids and to expel the excess of the hydrogen peroxide. Finally make the solution acid with hydrochloric acid and determine the sulfuric acid as barium sulfate.

This method yields excellent results and can be applied to the

Determination of Sulfur in Iron and Steel

Inasmuch as the amount of sulfur present is small, a large amount of the substance must be taken for the analysis. For pig iron 2–5 g are sufficient; for steel 5 g, and for wrought iron as much as 10 g, should be used.

* Prepare the hydrogen from zinc and sulfuric acid in a Kipp generator. Wash the gas first with an alkaline lead solution to remove traces of hydrogen sulfide and then with water.

† By the absorption of the hydrogen sulfide in the ammoniacal solution of hydrogen peroxide the latter is always colored somewhat yellow owing to the formation of a little ammonium disulfide. This yellow color can be distinctly seen in the delivery tube, where it dips into the solution in the receiver and later disappears owing to further oxidation:

$$(NH_4)_2S_2 \rightarrow (NH_4)_2S_2O_3 \rightarrow (NH_4)_2SO_3 \rightarrow (NH_4)_2SO_4$$

When the color can no longer be detected, it is a sign that the greater part of the hydrogen sulfide has been driven over.

The determination is carried out in the same way as before, except that the 6 N hydrochloric acid should not be diluted; allow the acid to act upon the iron without first covering it with water, and continue boiling for 10 minutes after the gas evolution has ceased and all the iron has dissolved.

Instead of collecting the evolved hydrogen sulfide in ammoniacal hydrogen peroxide, it is often more convenient to absorb it in ammoniacal cadmium solution, or in caustic soda solution, and determine the sulfur volumetrically by an iodometric process as will be described later.

Bamber Method for Determining Sulfur in Iron and Steel

On account of the uncertainty in obtaining all the sulfur present in iron or steel by the above evolution method, the Committee on Standard Methods for the Analysis of Iron of the American Foundrymen's Association have recommended the following method, which is that proposed by Bamber.

Dissolve 3 g of drillings in concentrated nitric acid. After the iron is completely dissolved, add 2 g of potassium nitrate, evaporate to dryness on the water-bath, and ignite the dry residue over an alcohol lamp to a red heat. After the ignition, add 50 ml of a 1 per cent solution of sodium carbonate, boil for a few minutes, and filter, washing the precipitate with hot 1 per cent sodium carbonate solution. Make the filtrate acid with hydrochloric acid and again evaporate to dryness. Moisten the residue with 2 ml of concentrated hydrochloric acid and add 50 ml of water. Heat to boiling and filter. Dilute the filtrate to 100 ml and precipitate hot with barium chloride solution.

During the determination great care should be taken to prevent the absorption of fumes containing sulfur. For this reason a gas flame should not be used at any stage in the process.

The following procedure is also recommended by the Bureau of Standards.

Dissolve 4.57 g of steel $\left(\frac{100 \times S}{3 \times BaSO_4}\right)$ by heating carefully with 50 ml of concentrated HNO_3. If the sample dissolves very slowly, add a little concentrated HCl dropwise at intervals. To the solution add 0.5 g of Na_2CO_3, evaporate carefully to dryness, and bake for 15 minutes on the hot plate. Cool, add 30 ml of concentrated HCl, and repeat the evaporation and baking. Now add 30 ml of concentrated HCl and evaporate to a sirup. Add 5 ml more of HCl and 5 g of 20–30 mesh zinc, free from sulfur. This serves to reduce the iron to ferrous salt which does not interfere as much as $FeCl_3$ does with the precipitation

of all SO_4^{--} as pure $BaSO_4$. Heat on the water-bath until all the ferric ions are reduced and the evolution of hydrogen has nearly ceased. Filter and wash with about 75 ml of 0.25 N HCl, added in small portions. Heat to about 70°, and add 10 ml of 10 per cent barium chloride solution. Allow to stand over night. Filter through an ashless filter; wash six times with hot N HCl and then with hot water until free from chloride. Ignite and weigh the $BaSO_4$. Run a blank on all the reagents going through all the above operations in exactly the same way. To find the per cent of sulfur, multiply the weight of the precipitate of $BaSO_4$ by 3.0.

The following method has also been found to give good results.

Meinicke Method for Sulfur in Iron and Steel

Dissolve 4.57 g of the metal in 25 ml of potassium-cupric chloride solution (300 g K_2CuCl_4 and 100 ml concentrated hydrochloric acid per liter). Filter off the residue, containing all the sulfur, using an asbestos filter. Wash 2 or 3 times with 5 per cent hydrochloric acid and then return residue and asbestos pad to the beaker and cover with 20 ml of concentrated nitric acid. Heat and add potassium chlorate until all carbonaceous matter is destroyed. Add 5 ml of concentrated hydrochloric acid to dissolve the precipitated manganese dioxide and again filter through asbestos. Evaporate the solution to dryness, take up in 10 ml of hydrochloric acid, and evaporate to dryness again. Take up in 10 ml of 2 per cent hydrochloric acid and 20 ml of water and filter through paper. Precipitate the sulfuric acid in the boiling filtrate, containing 1 per cent hydrochloric acid by volume, with 2 ml of hot 10 per cent barium chloride solution. Digest a short time on the hot plate and filter. Wash the barium sulfate with hot water until free from chlorides, ignite slowly, and weigh. The weight of barium sulfate in grams multiplied by 3 is equal to the percentage of sulfur. Run a blank on all reagents, carrying out every step of the procedure.

Method of Krug*

Dissolve 5 g of the metal in 50 ml of concentrated nitric acid. When all the iron has dissolved, add 0.25 g of potassium nitrate, evaporate to dryness, and bake the residue. Take up in hydrochloric acid and carry out the Rothe ether separation as described on p. 172. After removing the ether precipitate the sulfuric acid with hot barium chloride reagent.

* *Stahl und Eisen*, **25**, 887 (1905).

Colorimetric Determination of Sulfur in Iron and Steel*

Principle. — The hydrogen sulfide evolved from a weighed sample is passed through a cloth which has been wet with a solution of cadmium acetate. The hydrogen sulfide reacts with the cadmium salt to form yellow cadmium sulfide, and the intensity of the color is proportional to the amount of hydrogen sulfide.

If a grams of substance produce a certain shade then it would take $2a$ grams of a substance containing half as much sulfur to duplicate it, or in other words, the relations hold, $as = a's'$, where a and a' represent the amount of substance taken for the analysis and s and s' the percentage of sulfur present. In the first place, then, a scale must be prepared of different shades representing different percentages of sulfur. For this purpose, Wiborgh uses the apparatus shown in Fig. 64. It consists of a 250–300 ml Erlenmeyer flask A with a side-arm funnel T and with a ground-glass connection between the cylinder B and A. B is about 20 cm long, and is from 5.5 to 6.0 cm wide at the top and about 8 mm at the bottom; the upper edge is rounded over and ground perfectly smooth. Upon this upper edge are placed two rubber rings of the same inner diameter as the glass cylinder. Between these two rings is laid a circular piece of cloth C that has been dipped in a solution of cadmium acetate, and upon the upper rubber ring is placed a wooden ring H which is held firmly against the edge of the cylinder by means of three clamps K (only two are shown in the illustration).

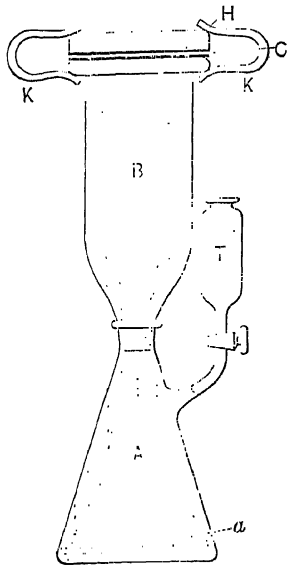

FIG. 64.

Fill the flask A not quite half full with distilled water, boil a few minutes to remove the air, take away the flame, and drop into the flask a weighing-tube containing a definite amount of a sample whose sulfur content is known. Insert the cylinder, with the cadmium acetate cloth in position in the neck of the flask, and boil gently until the cloth is uniformly moistened with the aqueous vapor which is seen to pass through it. The water must not be boiled too strongly and the cloth must not be allowed to puff up, for in that case it will become distorted and afterward an unevenly colored surface will be obtained. After

* J. Wiborgh: *Stahl und Eisen,* 6 (1866), 240.

boiling for 3 or 4 minutes, cautiously add 6 N sulfuric acid, drop by drop, to the contents of the flask (3 ml for each 0.1 g of iron) through the funnel T. The evolution of hydrogen sulfide begins at once and is recognized by the cadmium acetate cloth becoming yellow. After all the acid has been added, continue boiling until no more gas is evolved from the substance, and then for 10 minutes more in order to expel it from the solution completely.

Now remove the piece of cloth and place it upon a piece of white filter paper, so that the side which was toward the flask is on top. In the same way prepare a scale of six different shades corresponding to 0.02 mg, 0.04 mg, 0.08 mg, 0.12 mg, 0.20 mg, and 0.28 mg of sulfur, etc. For the determination proper, weigh out from 0.1 to 0.8 g of the substance (according to its supposed sulfur content) and treat in the same way. If with a sample of 0.2 g a shade corresponding to Tint No. 5 is obtained, the sample contains 0.2 mg of sulfur.

Remark. — The above process is very simple and to be recommended if a large number of sulfur determinations are to be made, as in iron and steel laboratories. It is to be noted, however, that an accurate value is obtained only when all the sulfur is present in a form such that it is evolved as hydrogen sulfide on treatment with acid.

IV. Determination of Sulfur in Insoluble Sulfides

For this analysis the sulfur is either oxidized to sulfuric acid and determined as barium sulfate, or the sulfide is converted into a soluble sulfide which is analyzed as described above.

The oxidation of the sulfide can take place:

(*a*) *In the Dry Way.*
(*b*) *In the Wet Way.*

(A) OXIDATION IN THE DRY WAY

1. *Fresenius' Method: Fusion with Sodium Carbonate and Potassium Nitrate*

Intimately mix 0.5 g of the finely powdered sulfide in a spacious nickel crucible with 5 g of sodium carbonate and 1.25 g of potassium nitrate, cover with a thin layer of sodium carbonate, and heat at first gently, then strongly until the contents of the crucible are melted; keep at this temperature for 15 minutes. After cooling, extract the melt with water, filter, boil the residue with 2 per cent sodium carbonate solution, and finally wash with water to the disappearance of the alkaline reaction. To the filtrate in a covered beaker add an excess of hydrochloric acid, boil, expel carbon dioxide, and evaporate to dryness. To remove all the nitric acid, treat the dry mass with 10 ml concen-

trated hydrochloric acid, and again evaporate to dryness. Moisten this last residue with 1 ml of concentrated hydrochloric acid, add 100 ml of water, heat to boiling, and filter. Dilute the filtrate to 350 ml, heat to boiling, and precipitate with 24 ml of normal barium chloride solution which is diluted to 100 ml and added as quickly as possible while stirring vigorously (cf. Sulfuric Acid).

2. *Sodium Peroxide Method**

The above method has long been accepted as a standard one for determining sulfur in pyrite and other insoluble sulfides, but equally good results can be obtained by substituting sodium peroxide as the oxidizer, and the procedure is shorter.

Procedure. — Mix 0.5 g of pyrite with 5 g of pure sodium peroxide and 4 g of sodium carbonate in a nickel or iron crucible. Cut an opening in a piece of asbestos board (at least 4 inches square) sufficiently large to allow two-thirds of the crucible to project below the asbestos. The purpose of this shield is to keep the products formed by the combustion of the gas from reaching the mouth of the crucible. Heat the contents of the crucible gently for 10 minutes so that the mass softens and bakes together and then raise the temperature until the crucible is exposed to the full heat of the Tirrill burner for 20 minutes.

Allow the contents of the crucible to cool and place in a small beaker with 150 ml of hot water. When the sodium salts are all dissolved, remove the crucible and add 5 ml of a saturated solution of bromine in concentrated hydrochloric acid. The purpose of the bromine is to make sure that the oxidation of the sulfur is complete.† It is necessary to add acid, because otherwise the hot sodium hydroxide solution is likely to destroy the filter paper. After heating to boiling, filter the solution and wash the residue of ferric hydroxide free from sulfate.

Carefully neutralize the filtrate with $6N$ hydrochloric acid, and add 2 ml in excess. Heat the solution till all the bromine is expelled, dilute to 350 ml, heat to boiling, and precipitate with 24 ml of normal barium chloride solution which is diluted to 100 ml and added slowly while stirring vigorously. Filter, wash, ignite and weigh the barium sulfate precipitate in the usual way (cf. Sulfuric Acid).

* W. Hempel, *Z. anorg. Chem.*, **3**, 193 (1893); J. Clark, *J. Chem. Soc.*, **63**, 1079 (1893); Höhnel, *Arch. Pharm.*, **232**, 222; C. Glaser, *Chem.-Ztg.*, **18**, 1448; Fournier, *Revue générale de chimie, pure et appliquée*, **1903**, 77; List, *Z. angew. Chem.*, **1903**, 414.

† A black residue may denote ferrous sulfide or nickelic oxide. It may be tested for sulfur by dissolving in hydrochloric acid and bromine and adding barium chloride to the diluted solution.

3. *Oxidation by Chlorine* (*Rose*)

This important method is used less to determine the amount of sulfur present in insoluble sulfides than to effect the solution of the sulfide for the separation and determination of the metals. As an example of this sort of an analysis we will consider the

Analysis of Tetrahedrite (Fahlerz)

Tetrahedrite is a complex sulfide corresponding to the general formula $4\,MS \cdot R_2S_3$, in which M is Cu_2, Ag_2, Fe, Zn, or Hg_2, and R is As, Sb, or Bi.

Place 0.5–1.0 g of the powdered substance into a porcelain boat *S*,

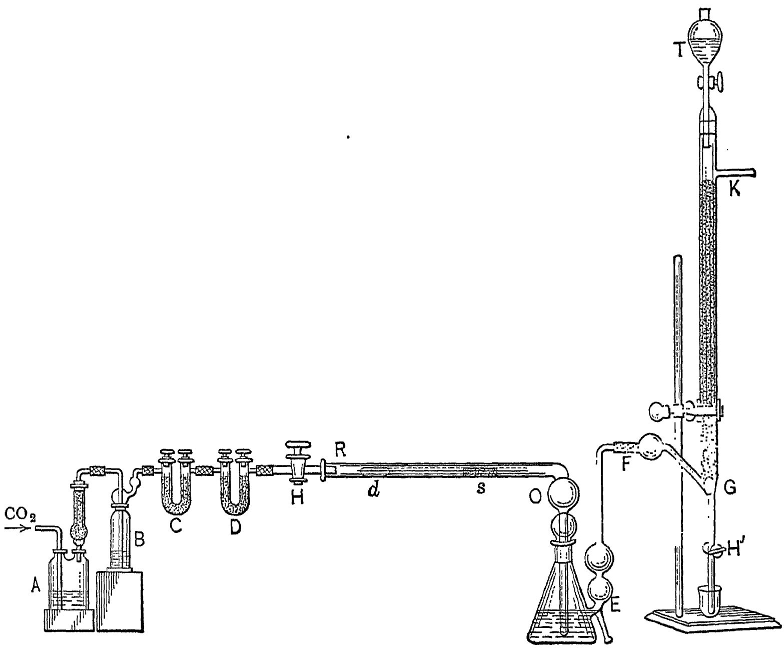

FIG. 65.

Fig. 65, shove this into the decomposition tube *R* and also insert the diffusion tube, *d*, which is just small enough to fit into *R*. Both ends of *d* are sealed so that the tube *R* is nearly stopped up at this point. Put the decomposition tube into a drying-closet, as shown in Fig. 52, p. 218, and connect one end through the stopcock *H* with the purification tubes *A*, *B*, *C*, and *D* and the other end with the vessels *E* and *G*. The flask *E* contains 100 ml of 2.5 *N* hydrochloric acid and 3.5 g of tartaric acid, and the Landolt tube *G* contains a column of glass beads

upon which hydrochloric and tartaric acid mixture trickles from the funnel T during the entire experiment. Conduct a slow, steady stream of chlorine through the apparatus without heating. Generate the chlorine by the action of hydrochloric acid upon bleaching powder in a Kipp generator. Pass the gas through the wash-bottle A containing water, the bottle B containing sulfuric acid, and the tubes C and D containing pieces of calcite to remove traces of acid. The action of the chlorine upon the substance generates heat and the decomposition at once starts. The volatile chlorides to some extent reach the flask E but condense also in O and in the front end of the tube outside the drying-closet. By careful heating with a small flame, it is easy to drive the condensed chlorides into the receiver. Allow the contents of the tube to cool in the stream of chlorine and finally drive out the chlorine with carbon dioxide. Then remove the diffusion tube d and the boat. Loosen the connection with the Landolt tube, and by blowing at F cause acid to flow into O several times. Then wash out the entire contents of the tubes into E with hydrochloric-tartaric acid mixture.

The Residue A

consists of silver, lead, and copper chlorides, almost all of the zinc, lead, considerable amounts of iron, and the gangue.

The Solution B

contains all the sulfur as sulfuric acid, the bismuth as chloride, the arsenic and antimony as their pentoxide compounds, a part of the iron and zinc, and often small amounts of lead.

Treatment of the Residue A

Heat this for some time with $6N$ hydrochloric acid, finally dilute with water, allow to settle, and filter off the residue consisting of silver chloride and the gangue. Wash thoroughly with hot water to make sure that all lead chloride is removed, treat with ammonia on the filter and precipitate the silver from the ammoniacal filtrate by acidifying with hydrochloric acid, and determine as the chloride. Ignite the residue, insoluble in ammonia, wet in a platinum crucible, and weigh.

Into the filtrate from the silver chloride, pass hydrogen sulfide until the solution is saturated. Filter off the precipitate of copper and lead sulfides and separate the lead from the copper according to p. 207. Combine the filtrate from the hydrogen sulfide precipitate with that obtained from Solution B after hydrogen sulfide has been passed into it.

Treatment of Solution B

Pass a stream of carbon dioxide through the solution for some time to remove the greater part of the excess of chlorine, and then saturate with hydrogen sulfide at the temperature of the water-bath after standing 12 hours. Filter off the precipitate of arsenic, antimony, mercury, and possibly bismuth sulfides. Separate the arsenic and antimony from the mercury and bismuth by means of ammonium sulfide as described on p. 229. From the ammonium sulfide solution precipitate the arsenic and antimony by acidifying with dilute hydrochloric or sulfuric acid, filter off the precipitated sulfides, and separate the arsenic from the antimony as described on pp. 233 *et seq.*

The precipitate insoluble in ammonium sulfide usually consists almost entirely of mercuric sulfide and sulfur, in which case, wash it first with alcohol, then a few times with carbon bisulfide, then with alcohol again, dry at 110° C, and weigh. If bismuth is present, however, treat the mixture of the two sulfides with 6 N nitric acid. Boil, add an equal volume of water, filter off the residue, and determine the bismuth in the filtrate according to p. 189, and the mercury as just described.

The filtrate from the hydrogen sulfide precipitate contains iron and zinc. Combine it with the corresponding filtrate from the Residue A, which likewise contains these metals. Precipitate by the addition of ammonia and ammonium sulfide, filter off, dissolve the precipitate in 2 N hydrochloric acid, oxidize the solution with nitric acid, and separate the iron from the zinc, preferably by the basic acetate method (see p. 158).

It is best to determine the sulfur in a separate portion by fusion with sodium carbonate and peroxide as described on p. 328.

The determination of the sulfur in an aliquot part of the Solution B is not to be recommended on account of the fact that the metals present are likely to contaminate the precipitate of barium sulfate.

(B) OXIDATION IN THE WET WAY

For this purpose aqua regia, fuming nitric acid, bromine, hydrochloric acid and potassium chlorate, and, in some cases, ammoniacal hydrogen peroxide have been proposed.

Aqua regia is most frequently used in practice and in the proportion first recommended by J. Lefort,* viz., 3 volumes of nitric acid, *d.* 1.4, and 1 volume of hydrochloric acid, *d.* 1.2. As an example we will cite the

* *J. Pharm. de Chimie* [IV], **9**, 99, and *Z. anal. Chem.*, **9**, 81.

Determination of Sulfur in Pyrite, G. Lunge's Method

The sample should be finely ground, but it must be borne in mind that rapid grinding in the air may generate enough heat to cause the oxidation of some sulfur so that an appreciable amount escapes as dioxide. Of the fine powder, treat 0.5 g with 10 ml of a mixture consisting of 3 parts nitric acid, *d.* 1.42, and 1 part hydrochloric acid, *d.* 1.2, in a 300-ml beaker which is covered with a watch glass. At first allow the acid to act upon the pyrite in the cold, but finish by heating upon the water-bath. If sulfur separates, oxidize it with a very little powdered potassium chlorate. Transfer the solution to a porcelain evaporating-dish and evaporate to dryness on the water-bath. Treat the residue with 5 ml of concentrated hydrochloric acid and again evaporate to dryness. Moisten the dry mass now with 1 ml of concentrated hydrochloric acid and 100 ml of hot water, filter through a small filter, and wash the residue first with cold water and then with hot water. To the hot filtrate, if not more than 150 ml in volume, add ammonia till the odor persists and then 30 ml of $3N$ ammonium hydroxide in excess to prevent the formation of any basic ferric sulfate. Keep at about 70° for 15 minutes. Filter off the ferric hydroxide precipitate and wash with hot water, each time churning up the precipitate, until a volume of about 400 ml is reached. Neutralize the filtrate with hydrochloric acid, using methyl orange as indicator, and add 1 ml of concentrated hydrochloric acid in excess. Heat just to boiling and add 100 ml of boiling-hot, $0.2N$ barium chloride solution while stirring vigorously.

Wash the barium sulfate precipitate 3 times by decantation with boiling water, then transfer to a filter and wash free from chlorides, ignite, and weigh.

To test the ammonia precipitate for sulfur, transfer it from the filter into a beaker by means of a stream of water from the wash-bottle and dissolve it by the addition of as little hydrochloric acid as possible. To the resulting solution add an excess of ammonia, filter and test the filtrate and washings as in the main analysis. Should any barium sulfate be obtained in this way, it should be filtered off and weighed with the main part of the barium sulfate precipitate.

Remark. — It is still better to filter the precipitate through a Munroe or Gooch crucible. After washing, dry the precipitate as much as possible by suction, place the crucible within a larger porcelain or platinum crucible, heat gently, cool and weigh.

The above method gives excellent results, which as a rule agree closely with those obtained by the preceding method. If the pyrite, however, contained barium or any considerable amount of lead, some sulfate will always remain undissolved with

the gangue. In such cases the Lunge method will give lower results but on the other hand it represents more nearly the quantity of sulfur in the pyrite which is available for the manufacture of sulfuric acid. In spite of the strong oxidizing power of the above mixture of nitric and hydrochloric acids, it is not sufficient to permit the determination of sulfur in roasted pyrite, on account of the danger of losing some sulfur as hydrogen sulfide. Such products should be fused with sodium carbonate and peroxide as previously described.

In carrying out the Lunge method, often a little sulfur separates in dissolving the sample. It has been recommended to dissolve this sulfur by adding potassium chlorate but when this is done the results are likely to be high. To overcome this difficulty, Allen and Bishop recommend dissolving the pyrite in a mixture of bromine and carbon tetrachloride. The latter dissolves any sulfur that is liberated and the dissolved sulfur is easy to oxidize.

Determination of Sulfur in Pyrite. Method of Allen and Bishop*

Weigh 0.5495 g of sample, ground to pass an 80-mesh sieve, into a tall beaker of 300–400 ml capacity, and add 6–8 ml of a solution of 2 vols. liquid bromine in 3 vols. of pure carbon tetrachloride (free from sulfur). Cover the beaker and allow to stand 15 minutes at the room temperature with occasional gentle shaking. Add 10 ml of concentrated nitric acid and digest in the same way for another 15 minutes. Heat at a temperature below 100° until all action has ceased and most of the excess bromine has been expelled. Raise the cover glass and evaporate to dryness. Cover the residue with 10 ml of concentrated hydrochloric acid, again evaporate to dryness, and heat the contents of the covered beaker for at least 30 minutes at 100°.

Moisten the residue with 1 ml of concentrated hydrochloric acid and dilute with 50 ml of water, washing the cover glass and the sides of the beaker. Heat until all the ferric salt is dissolved, and allow to cool for 3 minutes.

Reduce the iron by adding 0.1 g of powdered aluminum, shaking the contents of the covered beaker to bring the metal in contact with all parts of the solution. Sufficient aluminum should be added to reduce all the iron to the ferrous condition, but any considerable excess is to be avoided.

When the reduction of the iron is complete, as shown by the color of the solution, and the solution has cooled sufficiently so that there is no noticeable "misting" in the beaker, filter off the silica and the excess aluminum and wash with water until free from chloride. Dilute with cold water to a volume of 650 ml, add 5 ml of 6 N hydrochloric acid, and stir thoroughly. To the cold solution slowly introduce, while stirring, 50 ml of cold 5 per cent barium chloride solution in single

* *J. Ind. Eng. Chem.*, **11**, 46 (1919).

drops, at the rate of about 5 ml per minute. Allow the precipitate of barium sulfate to settle at least 2 hours and preferably over night. Filter, wash with cold water till free from chloride, dry, ignite, and weigh in the usual manner. The weight of the precipitate multiplied by 25 gives the percentage of sulfur.

Determination of Sulfur in Coal, Eschka Method*

If sulfur compounds are heated with a mixture of magnesium oxide and sodium carbonate, all the sulfur can be converted into water-soluble sulfate. It is generally assumed that air is the oxidizing agent and the heating is usually accomplished in an open dish. Recently, however, the use of a porcelain or platinum crucible has been advocated and the results appear to be equally good, which indicates that the oxidation of the sulfur may be accomplished as a result of the reduction of the carbonate. The magnesium oxide prevents the mass from fusing and apparently also catalyzes the oxidation which, however, is not as rapid as when an oxidizing flux is used.

Prepare Eschka's ignition mixture by mixing 2 parts of light calcined magnesium oxide with 1 part of anhydrous sodium carbonate, both free from sulfur. Mix 1 g of 60-mesh coal with 3 g of the Eschka mixture on a sheet of glazed paper. Transfer to a porcelain, silica, or platinum dish, or to a spacious crucible, and cover with about 1 g of the Eschka mixture.

Heat slowly with an alcohol flame until most of the volatile matter has been driven off, then gradually raise the temperature and heat with the full flame of the burner for 30 minutes or more, stirring occasionally, until all the black particles have been oxidized.

After the ignition, rinse the material into a 200-ml beaker, add 100 ml of hot water, and digest on the steam-bath for 30 minutes with occasional stirring. Filter and wash the insoluble residue thoroughly with hot water. The filtrate and washings should total about 250 ml. Add 20 ml of saturated bromine water, stir, make slightly acid with hydrochloric acid, and boil till the excess bromine is removed and the solution is colorless. To the boiling solution add dilute barium chloride solution (20 ml of a 5 per cent solution) and allow to stand at least 1 hour before filtering. Ignite and weigh the barium sulfate.

(C) HYDROGEN SULFIDE FROM INSOLUBLE SULFIDES

(a) *The Iron Method*†

In 1881, M. Gröger showed that by heating pyrite with iron out of contact with the air the former is quantitatively changed into ferrous sulfide

$$FeS_2 + Fe = 2\ FeS$$

* *Chem. News* **21**, 261 (1870).

† *Ber.*, **24**, 1937 (1891).

and from the latter all the sulfur will be given off as hydrogen sulfide on treatment with hydrochloric acid. The following method is suitable not only for the analysis of pyrite but for all other insoluble sulfides.

Procedure. — First of all heat the finely powdered sulfide out of contact with the air with iron powder. In this way part of the sulfur is usually given up to the iron, and the compound itself is reduced to compounds which are acted upon by hydrochloric acid with evolution of hydrogen sulfide; the latter can be absorbed in ammoniacal hydrogen peroxide solution, as described on p. 322. Heat with the iron in a small glass crucible about 30 mm long and 10 mm in diameter (Fig. 63, *b*), which can be easily made from an ordinary piece of combustion tubing. Place in the crucible about 3 g of iron powder that has been previously ignited in hydrogen, mix with it 0.3–0.5 g of the sulfide, and cover the mixture with a thin layer of iron powder. Place the crucible in the opening of the piece of asbestos board *A* (Fig. 63, *b*) and upon it place the gas-delivery tube *B* which has been prepared from difficultly fusible glass. Pass a stream of dry carbon dioxide* through the apparatus for a few minutes and gently heat the crucible with a small flame. Usually a distinct glowing is visible, but no trace of the sulfur is lost by volatilization. As soon as the contents of the crucible have ceased to glow, raise the temperature until a dull red heat is obtained, and keep the crucible at this temperature for 10 minutes.

After cooling in the carbon dioxide, place the crucible together with its contents in the 400-ml flask *K* and connect with the absorption vessels *V* and *P* as shown in the figure. The rest of the procedure is carried out as described on p. 322.

Remark. — Commercial iron powder always contains a small amount of sulfur, so that a blank experiment must be made with a weighed amount of the powder, and the same quantity of iron used for the experiment proper. Subtract the amount of sulfur found to be present in the iron from the amount found in the analysis.

The author was disappointed in not being able by this method to distinguish between the sulfur present in insoluble sulfides as sulfide and that present as sulfate (barium sulfate). If the amount of sulfate present is small, it is completely reduced to sulfide by this method; if a large amount of sulfate is present, it is often only partially reduced. As the amount of barium sulfate† present in insoluble sulfides

* Prepare the carbon dioxide from marble and hydrochloric acid in a Kipp generator. To purify the gas pass it through a wash-bottle containing water, then through one containing potassium permanganate, then through a tube filled with pumice soaked in copper sulfate solution, and finally through a calcium chloride tube. Potassium permanganate and copper sulfate serve to remove traces of hydrogen sulfide that the carbon dioxide might contain.

† Only barium sulfate is reduced with difficulty; the sulfates of the heavy metals are easily reduced.

is usually small, however, this method serves for the determination of practically all the sulfur.

(*b*) *The Tin Method**

Principle. — Almost all insoluble sulfides on being treated with metallic tin and concentrated hydrochloric acid give off their sulfur as hydrogen sulfide. Harding,† who first studied this method, used tin and hydrobromic acid.

Procedure. — In the evolution tube (Fig. 66), which is 20 cm long and 2.5 cm wide, place a layer of finely powdered tin (*g*) about 0.5 cm thick. Upon this place the substance enclosed in tinfoil (*s*) and then a layer of granulated tin *Z* about 6 cm deep. Pass a current of pure hydrogen through the apparatus for about 5 minutes, after which close the stopcock and connect the tube with the receivers *P* and *V*, as shown in the figure. The flask *V* contains an ammoniacal solution of hydrogen peroxide, but *P* contains 2–3 ml of water to remove any stannous chloride that may be carried over with the gas. Add concentrated hydrochloric acid through the drop-funnel until the tin is at the most half covered with the acid. Heat the contents of the tube slightly, preferably by placing it in a small paraffin-bath. The capsule of tin soon dissolves, and the substance is seen to be floating in the acid. It dissolves after about 15 minutes, and the acid becomes perfectly clear. Continue heating until no more yellow coloration can be detected in the delivery tube which dips into the receiver *V*. Then add more acid to the contents of the tube, until the tin is completely covered, and heat for half an hour longer, meanwhile heating the contents of *P* to boiling and passing a current of hydrogen through *a*. By this means all the sulfur will be driven over into *V*‡ and there held in solution as ammonium sulfate and analyzed as described under Sulfuric Acid, Method of Hintz and Weber.

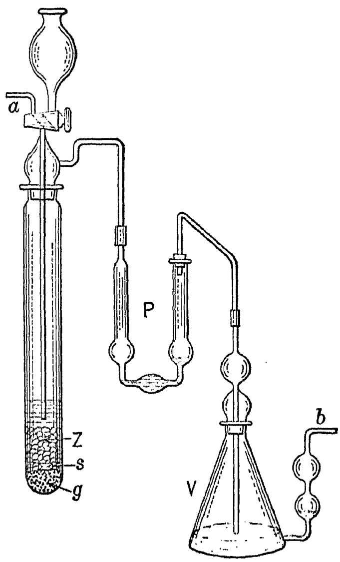

FIG. 66.

* *Ber.*, **25**, 2377.

† *Ber.*, **14**, 2085.

‡ With large amounts of sulfur, one receiver is often insufficient. In such cases connect the tube *b* with a Péligot tube containing ammoniacal hydrogen peroxide as shown in Fig. 63, p. 323.

Remark. — This method affords an accurate means for determining the sulfur present in insoluble sulfides as sulfide in the presence of sulfate. Thus the amount of pyrite in clay-slate that contains gypsum can be determined by this method, although usually the treatment with aqua regia or fusion with soda and niter is used. By these last two methods, however, the *total* sulfur is determined. More accurate values for the *pyrite* present may be obtained by decomposition in a current of chlorine (see p. 329), in which case only the sulfide sulfur is determined.

Finally, it may be mentioned that arsenic sulfide may be decomposed by the above method, although a longer time is required than with pyrite, copper, chalcopyrite, galena, cinnabar, etc. Arsenopyrite, on the other hand, is either unacted upon or only decomposed with difficulty, while the iron method effects the decomposition with ease.

Determination of Sulfur in Non-electrolytes

To determine the amount of sulfur present in organic compounds, it is oxidized to sulfuric acid and determined as barium sulfate.

The oxidation is effected:

(*a*) *In the Wet Way.*
(*b*) *In the Dry Way.*

(*a*) *Oxidation in the Wet Way* (*Carius*)

This operation is conducted in precisely the same manner as was described on p. 304 for the determination of halogens, except that no silver nitrate is added to the contents of the tube. After the closed tube has been heated and opened, transfer its contents to a beaker, add hydrochloric acid, and evaporate to a small volume in order to remove the nitric acid; dilute with water to a volume of about 200 ml, precipitate hot with a boiling solution of barium chloride, and weigh as barium sulfate.

(*b*) *Oxidation in the Dry Way* (*Liebig*)

Melt a mixture of 8 parts of potassium hydroxide (free from sulfate) and 1 part of potassium nitrate in a large silver crucible with the addition of a little water. After cooling, add a weighed amount of the substance and heat the contents of the crucible again very gradually, frequently stirring the mixture with a silver wire until the organic substance is completely decomposed. Cool, dissolve the melt in water, make acid with hydrochloric acid, and precipitate the sulfuric acid formed.

This method is particularly suited for the determination of sulfur present in difficultly volatile substances, *e.g.*, in wood-cements.

ACETIC ACID, $\begin{array}{c} CH_3 \\ | \\ COOH \end{array}$. Mol. Wt. 60.03

Free acetic acid is always determined volumetrically. For the analysis of acetates, the substance is heated with phosphoric acid when the free acetic acid distils over and is then titrated (cf. Part II, Acidimetry). The carbon and hydrogen of the acetate can be determined by Elementary Analysis (which see).

CYANIC ACID, HOCN. Mol. Wt. 43.02

The only method for examining cyanates consists of determining the amount of carbon and nitrogen present by a combustion (see Elementary Analysis).

Determination of Cyanic Acid, Hydrocyanic Acid, and Carbonic Acid in a Mixture of their Potassium Salts

In one portion of the substance determine the carbonic acid by adding calcium chloride to the ammoniacal solution and weighing the ignited precipitate as calcium oxide.

In a second portion determine the cyanogen of the cyanide as silver cyanide by treating the aqueous solution with an excess of silver nitrate, acidifying with nitric acid and determining the weight of the silver cyanide as described on p. 313.

In a third portion determine the potassium by evaporating with sulfuric acid and weighing the residue of potassium sulfate as described on p. 57. If from the total amount of potassium present the amount present as potassium carbonate and potassium cyanide is deducted, the difference gives the amount of potassium combined with the cyanic acid.

HYPOPHOSPHOROUS ACID, H_3PO_2. Mol. Wt. 66.05

Forms: Mercurous Chloride, Hg_2Cl_2; Magnesium Pyrophosphate,

(*a*) Determination as Mercurous Chloride

Treat the solution of the salt, which is slightly acid with hydrochloric acid, with an excess of mercuric chloride; by this means insoluble mercurous chloride is precipitated. After standing for 24 hours in a warm, dark place filter off the precipitate through a Gooch crucible, wash with water, dry at 110°, and from the weight of the mercurous chlo-

ride calculate the amount of hypophosphorous acid present as follows:

$$H_3PO_2 + 2\,H_2O + 4\,HgCl_2 = 2\,Hg_2Cl_2 + 4\,HCl + H_3PO_4$$

$$x = \frac{H_3PO_2 \cdot p}{2\,Hg_2Cl_2}$$

in which p is the weight of the Hg_2Cl_2 obtained in the analysis.

(*b*) Determination as Magnesium Pyrophosphate

First convert the hypophosphorous acid into phosphoric acid by adding 5 ml of concentrated nitric acid to the aqueous solution of 0.5–1 g of the substance in about 100 ml of water,* evaporating on the water-bath to a small volume, adding a few drops of fuming nitric acid, and again heating. After this, precipitate the phosphoric acid by magnesia mixture and ammonia and weigh the precipitate as magnesium pyrophosphate as described under Phosphoric Acid.

GROUP III

SULFUROUS, SELENIOUS, TELLUROUS, PHOSPHOROUS, CARBONIC, OXALIC, IODIC, BORIC, MOLYBDIC, TARTARIC, AND META- AND PYROPHOSPHORIC ACIDS

Sulfurous Acid, H_2SO_3. Mol. Wt. 82.08

Form: Barium Sulfate, $BaSO_4$

The sulfite, or free sulfurous acid, is first oxidized to sulfuric acid and then precipitated with barium chloride. The oxidation can be accomplished by means of chlorine, bromine, hydrogen peroxide, or potassium percarbonate.

Oxidation with Chlorine or Bromine

Allow chlorine water, or bromine water, to flow gradually into the aqueous solution of sulfurous acid, or of a sulfite; after the oxidation is complete, expel the excess of the reagent by boiling and precipitate the sulfuric acid with barium chloride.

Oxidation with Hydrogen Peroxide†

Treat the solution of sulfurous acid, or of a sulfite, with an excess of ammoniacal hydrogen peroxide, heat to boiling to remove the excess of

* If the hypophosphite were at once treated with nitric acid, metaphosphoric acid would be obtained; by the addition of water the ortho-salt is formed.

† The hydrogen peroxide should always be tested to see if it contains sulfuric acid; if it is found to be present, determine the amount and afterward use an accurately measured quantity for the oxidation. Deduct the amount of sulfuric acid from the peroxide from the total value found in the analysis.

the peroxide, make acid with hydrochloric acid, and precipitate with barium chloride.

With potassium percarbonate a similar procedure is used. Treat the cold alkaline solution of the sulfite with solid potassium percarbonate, heat gently, and gradually raise the temperature till the boiling point is reached. Then make acid with hydrochloric acid and precipitate with barium chloride.

Sulfurous acid may be determined very accurately by a volumetric analysis (cf. Part II, Iodometry).

Selenious and Tellurous Acids

The analysis of these acids was discussed under Selenium and Tellurium.

PHOSPHOROUS ACID, H_3PO_3. Mol. Wt. 82.05

Forms: Mercurous Chloride, Hg_2Cl_2, and Magnesium Pyrophosphate, $Mg_2P_2O_7$

This determination is effected exactly like that of hypophosphorous acid (cf. p. 338).

In this case, however, it is to be noted that 1 mole of Hg_2Cl_2 corresponds to 1 mole of H_3PO_3:

$$H_3PO_3 + 2\,HgCl_2 + H_2O = H_3PO_4 + 2\,HCl + Hg_2Cl_2$$

Determination of Phosphorous and Hypophosphorous Acids

In this case an indirect analysis must be made. After oxidizing one portion of the substance to phosphoric acid, determine the total phosphorus as magnesium pyrophosphate; allow mercuric chloride to act upon a second portion and determine the weight of mercurous chloride formed. From these data the amount of each acid present can be calculated as follows:

Assume that a solution containing the two acids is being analyzed. Let x denote the weight of hypophosphorous acid present in V milliliters of the solution.

Let m, n, o, and v represent the following chemical factors:

$$m = \frac{Mg_2P_2O_7}{2\,H_3PO_2} = 1.686 \qquad n = \frac{Mg_2P_2O_7}{2\,H_3PO_3} = 1.357$$

$$o = \frac{2\,Hg_2Cl_2}{H_3PO_2} = 14.30 \qquad v = \frac{\quad}{H_3PO_3}$$

Then ox is the weight of mercurous chloride produced from the hypophosphorous acid, and mx is the weight of magnesium pyrophos-

phate equivalent to the hypophosphorous acid. Further, let y represent the weight of phosphorous acid present in the same volume of the solution, vy the corresponding amount of mercurous chloride, and ny that of magnesium pyrophosphate. The total amount of the mercurous chloride is q, and the total amount of magnesium pyrophosphate is p. Then

$$mx + ny = p$$
$$ox + vy = q$$

from which it follows that

$$x = q\frac{n}{on - mv} - p\frac{v}{on - mv} = q \cdot 0.1399 - p \cdot 0.5933$$

and

$$\frac{\quad}{on - mv} - q\frac{\quad}{on - mv} = p \cdot 1.474 - q \cdot 0.1738$$

Carbonic Acid, H_2CO_3. Mol. Wt. 62.02

Carbonic acid is determined gravimetrically as CO_2; it can also be determined by measuring the volume of the gas or by titrating with an acid to determine the amount required to decompose a carbonate.

1. Gravimetric Determination of Carbon Dioxide

This analysis may be accomplished in two ways. From the weighed substance, the carbon dioxide can be expelled and the loss in weight determined. Second, the carbon dioxide may be expelled from a weighed amount of the substance and then absorbed in a suitable apparatus; in this case the carbon dioxide is weighed directly.

A. DETERMINATION OF CARBONIC ACID BY DIFFERENCE

(a) *Determination in the Dry Way*

For the analysis of a carbonate, or a mixture of carbonates which contains no volatile constituent other than the carbon dioxide, weigh out 1 g of the substance into a platinum crucible and gradually heat to a high temperature.* If calcium, strontium, or magnesium is present a final heating over the blast lamp or Méker is necessary; with other carbonates the heat of a good Tirrill burner is sufficient; even the difficultly decomposable cadmium carbonate can be analyzed by this method. The carbonates of barium and the alkalies, on the other hand, do not lose their carbon dioxide by such ignition.

* Carbonic acid cannot be determined by this method when the residual oxide suffers change, as, for example, in the case of $FeCO_3$ and $MnCO_3$ where an oxidation takes place.

If the substance contains water besides carbon dioxide, then the sum of the water + carbon dioxide is determined by the loss on ignition, and the amount of carbon dioxide is determined in a second portion by (*b*).

(*b*) *Determination in the Wet Way*

Principle. — Place the weighed carbonate in an apparatus containing acid, but in such a way that the substance does not at first come in contact with the acid. Then weigh the whole apparatus, and allow the acid to act upon the substance; carbon dioxide is evolved and escapes from the apparatus. (Care must be taken that no moisture escapes with the gas.) By afterward weighing the apparatus and subtracting this weight from that first obtained, the weight of the carbon dioxide is ascertained.

Procedure. — This analysis is easily accomplished, and a large number of different forms of apparatus have been devised for the purpose. In this book, however, only one of these so-called *alkalimeters* will be described, namely, that of Mohr, which in an improved form is shown in Fig. 67, although it must be stated that many other forms (*e.g.*, those of Bunsen,* Shrötter, Geissler, Fresenius-Will, etc.) answer the purpose equally well.

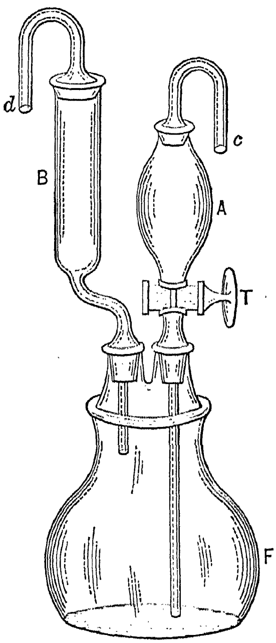

FIG. 67.

The alkalimeter consists of the small, wide-mouthed, flat-bottomed flask *F*, which has a ground-glass connection with the tubes *A* and *B*. At the bottom of *B* place a loose wad of cotton; insert a cylinder of glazed paper about 3 cm wide into the neck of the tube, and through this cylinder pour small pieces of sifted calcium chloride.† Remove the paper cylinder after the tube is about three-quarters full of calcium chloride, taking care that none of it adheres to the glass above the filled portion. Place another wad of cotton in the tube, insert the top part, and close the tube temporarily at *d* by means of a piece of stirring-rod within

* In the German edition of this book, Bunsen's alkalimeter is described instead of Mohr's. The above apparatus has the advantage of having a stopcock to separate the acid compartment from the flask, besides having a flat bottom, upon which it will rest unsupported. It is all made of very thin glass and is comparatively light.

† As commercial calcium chloride always contains a little free lime, some carbon

rubber tubing. The tube should be kept closed when not in use to prevent the gradual absorption of moisture from the air. Fill two ordinary calcium chloride tubes in the same way about two-thirds full, but in this case place softened cork stoppers at the end of the tubes after the second wad of cotton. Through a hole in each stopper introduce a short piece of glass tubing with rounded ends, and shove the cork far into the tube with the help of a stirring-rod, leaving the outer 2 or 3 mm empty. Fill this empty space in the tube with molten sealing-wax, so that a perfectly air-tight connection is made. Close these tubes, when not in use, by pieces of stirring-rod within rubber tubing.

Before beginning the determination the apparatus must be clean and dry. It is not advisable to dry the flask by washing with alcohol and ether, but it should be gently heated while a current of dry air is sucked through it. As aspirator an inverted wash-bottle may be used, from which the water is allowed to run out slowly through the shorter tube. During the aspiration the small calcium chloride tubes are connected with *c* and *d* respectively, so that no moisture can enter the flask.

When all is ready transfer 1–1.5 g of the finely powdered substance, from a weighing-tube, to the flask and add a little water.* Now fill the tube *A* two-thirds full with 2.5 *N* hydrochloric acid by means of a small funnel or thistle tube, and turn the stopcock *T* so that none of the acid will run into the flask. Place the whole apparatus, as shown in Fig. 67, upon the balance pan and accurately weigh. Remove from the balance; open the stopcock *T* so that the acid in *A* slowly drops into the flask. As soon as the evolution of carbon dioxide begins to take place quietly, allow the apparatus to stand without watching for 30 minutes. At the end of this time all the acid will have passed into the flask, and the decomposition will be nearly complete in most cases. It now remains to remove all carbon dioxide absorbed by the liquid and contained in the apparatus. This is effected by gently heating the solution by means of a small flame until the acid just begins to boil, meanwhile aspirating a current of dry air through *c* and out at *d*. Not more than three or four bubbles of air per second should be allowed to pass through the flask. As soon as the boiling begins, remove the flame and continue passing a slow current of air

dioxide will be absorbed by it and consequently low results obtained in the analysis, unless the calcium chloride is saturated with carbon dioxide before the analysis is made.

* This method is often used for the determination of the carbonic acid in baking-powders. Such substances are decomposed by water so that they should be kept dry until after the apparatus has been weighed.

through the apparatus until it is cold. Then stopper and allow to stand near the balance for half an hour or more, after which weigh it again without the stoppers. The loss in weight represents the amount of carbon dioxide originally present in the substance as carbonate.

Remark. — This method affords excellent results in the estimation of large amounts of carbonic acid, but it is unreliable for the analysis of small amounts such as are present in cements, etc. In such cases the Fresenius-Classen or Lunge-Marchlewski method is better. (See below and p. 352.)

The objection to this method lies in the fact that owing to the size and weight of the apparatus, there is likely to be an error in making the two weighings.* On the other hand, it is somewhat easier to expel carbon dioxide from a solution than it is to absorb it quantitatively. Before each weighing, dry the outside of the apparatus by wiping with a piece of chamois or clean linen.

B. DIRECT DETERMINATION OF CARBON DIOXIDE

Here again the determination can be carried out both in the dry and wet ways.

(a) *Determination in the Dry Way*

Weigh out 1–2 g of the substance into a porcelain boat, and shove the latter into the middle of a horizontally-held glass tube, about 20 cm long and 1–1.5 cm wide, and made of difficultly fusible glass. Both ends of the tube should be provided with calcium chloride tubes connected with it by means of tightly-fitting rubber stoppers. Through one of the calcium chloride tubes pass a slow stream of air (free from carbon dioxide)† and connect the other with two weighed soda-lime or ascarite tubes (cf. pp. 345, 362). Heat the substance gradually until it glows strongly, meanwhile passing a slow but steady current of air through the apparatus. When there is no further heat effect to be detected in the absorption tubes, allow the substance to cool in the current of air and subsequently weigh the tubes. The increase of weight represents the amount of carbon dioxide.

Remark. — This method can be employed for the analysis of all carbonates with the exception of those of barium and the alkalies,‡ though, of course, no other volatile acid can be present at the same time. Water is kept back by the calcium chloride tubes.

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* There is some danger of losing a little hydrochloric-acid gas during the operation. To prevent this the calcium chloride may be replaced by pumice impregnated with anhydrous copper sulfate, or the carbonate may be decomposed by means of sulfuric acid.

† The air is passed through two wash-bottles containing caustic potash solution.

‡ Even the carbonates of the alkalies and of barium can be analyzed in this way if they are mixed with potassium dichromate.

(b) *Determination in the Wet Way*

The apparatus for this determination is shown in Fig. 68. The decomposition flask *F* should have a capacity of about 250 ml; a wide-mouthed flask such as used for Soxhlet extractions is also suitable. The tube *T* of 8-mm diameter is made about 50 cm long and acts as an efficient air condenser. If a hole is blown at *E*, the flow

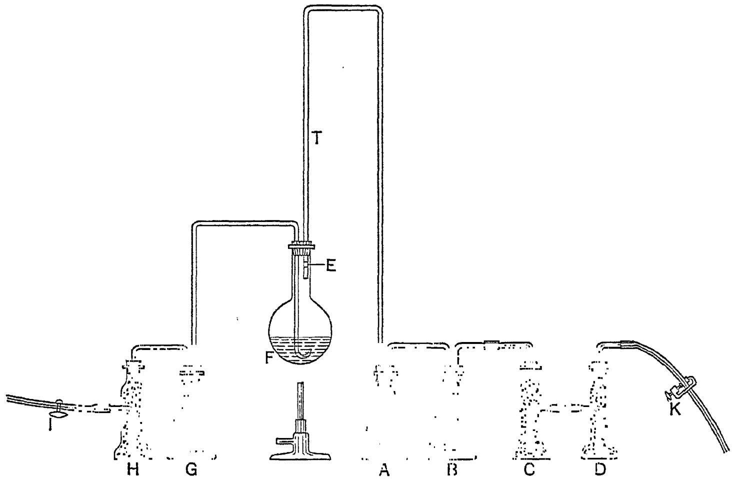


FIG. 68.

of gas from the decomposition flask is not impeded by condensed moisture during the experiment, but this is not very important.

A and *B* are Erlenmeyer flasks of 100–125 ml capacity. *A* is empty but *B* contains enough concentrated sulfuric acid to act as a bubble counter and to show whether the apparatus is tight. *C* is a Midvale absorption tube containing some drying agent such as *dehydrite*, $Mg(ClO_4)_2 \cdot 3H_2O$, between cotton plugs, and *D* is a similar tube containing ascarite (asbestos impregnated with NaOH) with cotton at the top and bottom. Instead of *dehydrite*, calcium chloride (of the grade marked "for drying tubes"), *anhydrone*, $Mg(ClO_4)_2$ or *desicclora*, $Ba(ClO_4)_2$, can be used.

By means of *K*, a small screw clamp on rubber tubing which is connected with suction, the rate of flow of gas through the apparatus can be regulated. *G* is another 100–125 ml Erlenmeyer flask which is, at the start, about half full of normal HCl. *H* contains ascarite. In the drawing a Midvale tube is shown at *H*, but a U-tube or any absorbing tower can be used equally well. The glass tubing that connects *F* and *G* should reach nearly to the bottom of each flask; it is well to make the tube a little narrower where it ends at the bottom of the flask *F* and to have the tip turned upward.

For decomposing the carbonate, sulfuric acid, hydrochloric acid, phosphoric acid, perchloric acid, and chromic acid have all been recommended. In the analysis of baking-powders, no acid is required because water alone causes the decomposition; in this case the flask *F* must be perfectly dry at the start.

If the substance contains besides the carbonate a sulfide which is decomposable

with acid, introduce before *a* and *b* a tube containing pumice impregnated with copper sulfate.* This serves to absorb all the hydrogen sulfide evolved.

Procedure. — First make sure that the apparatus is tight. Have the flask *G* empty but pour enough water in the flask *F* to seal the end of the tubing. Close the pinchcock *I* on the rubber tubing at the extreme left of the apparatus so that air cannot enter there, and make sure that all the rubber stoppers are inserted tightly in the necks of the four flasks. Open the screw clamp *K* a little and apply gentle suction so that at first about 2 bubbles of air per second will pass through the liquid in *B*. If the apparatus is tight the current of air will soon slow down. When the air is passing at the rate of about 1 bubble in 2 seconds, close *K* tightly and take the rubber tubing off the suction pipe. There should now be no movement of air through the liquids in *F* or *B*. After a few minutes, carefully allow air to enter the apparatus through the tubing at *I* by squeezing the end of the tubing to the left of *I* between the thumb and finger and alternately releasing the pressure at *I* and between the fingers. If the apparatus is tight, there will flow about as many bubbles of air through the apparatus as were withdrawn during the evacuation.

During this testing, the tube *D*, which has been wiped dry with a clean linen cloth, should be resting in the balance case. After it has been there at least 10 minutes, remove the rubber tubing from the ends of the capillary tubing and weigh it and its contents to 0.1 mg. Weigh accurately 0.5–0.6 g of carbonate into the dry flask *F*, and add enough water to seal the end of the tubing at the bottom of the flask. Connect the weighed ascarite tube to the front end of the train, place about 50 ml of approximately *N* hydrochloric acid in the flask *G*, and make sure that the pinchcock *I* is open. Apply gentle suction, and regulate the screw clamp *K* so that about 2 bubbles of gas per second pass through the sulfuric acid in *B*. When all the acid has been drawn from *G* into the flask *F*, start heating the contents of *F*. During the heating, watch the glass tubing that connects the flasks *F* and *G* and do not let the liquid pass from *F* toward *G*, as will happen if the liquid in *F* is heated too rapidly. If the liquid starts going toward *G*, turn down the flame and, if necessary, increase the suction. Finally boil the liquid in *F* for 1 minute. Then take away the flame and continue drawing air through the apparatus, at the rate of 2–3 bubbles per second, for 20 minutes longer, in order to get all the CO_2 into the absorption tube *D*. After this, detach *D* from the train and connect the two open ends with a piece of rubber tubing, to prevent absorption of CO_2 from the air.

* Cover 60 g of pumice pieces in a porcelain dish with a concentrated solution of 30–35 g of copper sulfate. Evaporate the solution to dryness with constant stirring and heat the residue at 150–160° for 4–5 hours.

Wipe the tube carefully with a piece of clean linen and allow it to stand in the balance case for 15 minutes. Remove the rubber tubing and weigh. The gain in weight represents absorbed CO_2.

Remark. — The results obtained by this method are perfectly satisfactory. For the analysis of substances containing small amounts of carbonate, take 3–10 g for the analysis. It is convenient to use another Midvale tube as a tare when weighing the tube *D*, then recording merely the difference in weight. Sulfites interfere with this determination, but the difficulty can be overcome by decomposing the carbonate with an excess of potassium dichromate solution and adding the dilute acid later.*

The following method is an example of the analysis of a commercial carbonate.

Analysis of Commercial White Lead†

If the sample is in the form of a paste, or is a mixed paint, it is necessary to find the

Percentage of Pigment. — Weigh 15 g of the paste into a weighed centrifuge tube. Add 20 ml of an extraction mixture made by mixing 10 volumes of ethyl ether, 6 volumes of benzene, 4 volumes of methyl alcohol and 1 volume of acetone. Mix thoroughly with a stirring-rod and wash off the rod with more of the extraction mixture, finally diluting to 60 ml with the same. Place the tube in a container of a centrifuge, surround with water, balance with a similar tube on the opposite arm and whirl at a moderate speed until the precipitate has settled well. Decant off the clear liquid and repeat the treatment with two more 40-ml portions of the extraction mixture and finally with 40 ml of ethyl ether. After pouring off the clear ether, remove the rest by placing the tube in a beaker of water heated to 80°. Finally dry 2 hours at 110°, cool, weigh, and calculate the percentage of pigment. Grind to a fine powder and pass through a No. 80 screen to remove skins. Preserve the dry sample in a glass-stoppered bottle.

* E. R. Marle, *J. Chem. Soc.*, **95**, 1491 (1909). If it is desired to determine a small quantity of carbon dioxide in a gas containing considerable hydrochloric acid and hydrogen sulfide, use a tube containing finely divided metallic copper, instead of the pumice and copper sulfate to absorb the hydrogen sulfide, and a tube containing *p*-nitroso-dimethylaniline to absorb hydrochloric acid, Vernon and Whitby, *J. Soc. Chem. Ind.*, **47**, 257 (1928).

† This method given here is based on the Tentative Methods of the American Society of Testing Materials and Circular No. 84 of the U. S. Bureau of Standards.

Total Lead and Insoluble Impurity. — Moisten 1 g of the pigment with water and dissolve in 25 ml of 6 N nitric acid in a covered beaker. Heat until all carbon dioxide is expelled, dilute and filter off any dissolved impurity. Dry at 110° and compute the percentage of insoluble matter. Add to the filtrate 20 ml of 18 N sulfuric acid, evaporate to fumes and determine the lead according to p. 185.

Metallic Lead. — Weigh 50 g into a 400-ml beaker, add a little water and 60 ml of 40 per cent acetic acid, taking care to avoid loss by effervescence. Heat to boiling, fill the beaker with water, decant off the solution, and digest the residue with 60 ml of a mixture of 360 ml of concentrated ammonium hydroxide, 1080 ml of water, and 2160 ml of 80 per cent acetic acid. Boil, fill the beaker with water, decant, and filter. Collect the residue on a watch glass and float off everything but the metallic lead. Dry at 110° and weigh.

Carbon Dioxide. — Take 1 g of the pigment and analyze as described on p. 346.

Acetic Acid. — Place 18 g of pigment in a 500-ml flask, add 40 ml of sirupy phosphoric acid, 18 g of zinc dust, and 15 ml of water. Distil through a Liebig condenser till only a small volume of liquid is left. With the condenser still in place, pass steam into the distilling flask until it is half full of condensed water, then distil again to a small volume. Repeat the steam treatment twice more. To the total distillate add 1 ml of sirupy phosphoric acid and distil down to 20 ml, using a splash trap between the flask and the condenser. Introduce steam until 200 ml of water condense in the distilling flask and again distil. To each 200 ml of distillate add phenolphthalein indicator solution and titrate with 0.1 N sodium hydroxide. Keep on distilling, with intermediate treatment with steam, until 10 ml of distillate require only 1 drop of 0.1 N alkali solution to color phenolphthalein. One milliliter of 0.1 N caustic alkali solution reacts with 0.006004 g of acetic acid or 0.005103 g of acetic anhydride.

Determination of Total Amount of Carbonic Acid in Mineral Waters

Place 3–4 g of freshly burnt lime* and the same amount of crystal-

* To prepare this lime absolutely free from carbonate, place the lime in a tube of difficultly fusible glass and heat in a small combustion furnace, meanwhile passing a current of dry air free from carbon dioxide over it. In this way 4 g of commercial lime can be freed from carbonate in 30–45 minutes. That the carbon dioxide is actually removed can be shown at the end of that time by passing the escaping air through baryta water; there should be no turbidity. A blank experiment should always be made with this lime. If it is desired to use commercial lime for the determination, determine the amount of carbonate present and use an accurately weighed amount for the analysis.

lized calcium chloride* in each of from 4–6 Erlenmeyer flasks whose necks are of such a size that they will each fit the apparatus shown in Fig. 68. Close the flasks by means of tightly fitting rubber stoppers and accurately weigh. Take a double-bored rubber stopper of such a size that it will fit into the neck of each of the above flasks and through one of the holes fit a short glass tube which reaches about 3 cm above the stopper and the same distance below, and through the other hole insert a glass tube about 50 cm long which likewise reaches about 3 cm below the stopper. To fill the weighed flasks with the water to be analyzed, take them to the spring, and fill one after another as follows: Replace the solid rubber stopper by the one fitted with the 2 tubes, hold the thumb over the shorter of the tubes, and dip the flask well below the surface of the water, but so that the longer tube still reaches into the air above. Now remove the thumb from the shorter tube; the spring-water will pass into the flask and the replaced air will escape through the long tube. As soon as the flask is almost full, again close the shorter tube with the thumb, remove the flask from the water, and once more quickly interchange the stoppers. To make sure that the solid stopper is not loosened while carrying the flask back to the laboratory, cover it with a piece of parchment paper, and tie it with string to the neck of the flask. Allow the flasks and contents to stand several days with frequent shaking. All the carbonic acid of the spring-water will then have reacted with the lime and be precipitated as calcium carbonate. Allow the precipitate to settle and weigh. The gain in weight represents the weight of water taken. Quickly pour off the supernatant liquid through a plaited filter, quickly throw the filter and its contents into the decomposition flask, connect with the train shown in Fig. 68, and determine the carbon dioxide as in the previous method.

This method is capable of yielding excellent results provided the flasks can be filled as above described. Often, however, the spring is not easily accessible, so that the flasks must be filled by a different method and usually a small amount of carbonic acid is lost during the operation. A much more expeditious and accurate procedure which can be performed within one hour at the spring, consists in the determination of the total amount of carbonic acid present in mineral waters by measuring the volume of the gas.†

* The addition of calcium chloride serves to decompose any alkali carbonate. This is not quantitatively decomposed by lime alone, particularly when magnesium carbonate is present.

† Cf. the modified method of Pettersson on p. 357.

2. Gas-volumetric Determination of Carbonic Acid

(a) *Method of O. Pettersson**

This excellent method, upon which the two following procedures are based, consists in evolving carbon dioxide from carbonates by the action of acid, collecting the gas over mercury and computing its weight from its volume. Pettersson's apparatus is shown in Fig. 69, and was used by him for the determination of the carbonic acid in sea-water and in carbonates, and also for the determination of carbon in iron and steel. The procedure for determining the carbonic acid in a water containing small amounts of free carbonic acid but considerable carbonate will suffice to show how the apparatus is used. Fill the decomposition flask *K* with distilled water up to the mark just below the side-arm (the mark is not shown in the illustration). By weighing the flask both empty and with this amount of water, the volume of the flask when filled to the mark is obtained. Drop in a small piece of aluminum wire† and connect the flask with the rest of the apparatus as shown in the figure. All the rubber tubing should be firmly fastened to the glass by means of wire. Close the cocks *a*, *b*, and *d*, open *c*, and remove the air in the measuring-tube by raising *M* until the mercury rises in the capillary up to the crossing point. After this close *c*, open *a*, lower *M*, and slowly open the screw-cock *d*. By this means the hydrochloric acid in *N* is introduced into the flask *K*. Allow the acid to run into the flask until the upper part of the apparatus is reached, then close *d* and *a*. Remove the air in the measuring-tube (which does not contain an appreciable amount of carbon dioxide) by opening *c* and raising *M*, after which again close *c*. Now once more open *a*, lower *M*, and heat the liquid in *K* by a flame.

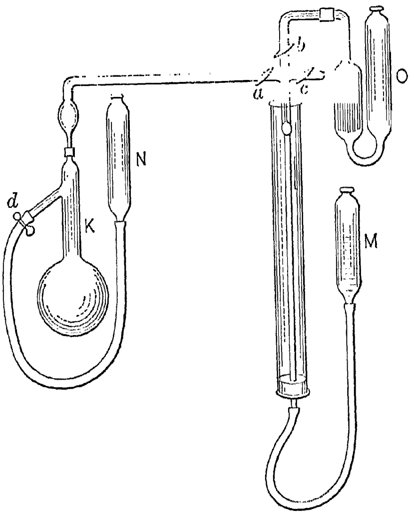


FIG. 69.

A lively evolution of gas at once ensues. As soon as the measuring-

* *Ber.*, **23**, 1402 (1890).

† At 720 mm and 15° C, 0.0142 g aluminum evolves 20 ml of moist hydrogen.

tube is almost filled with the gas, close *a*, remove the flame from under *K*, raise *M* until the mercury within it stands level with that in the measuring-tube, and read its position in the latter. At the same time note the barometer reading and the temperature of the cold water which surrounds the measuring-tube. After this open *b* and raise *M*, whereby the gas passes into the Orsat tube *O* which contains caustic potash solution (1:2). As soon as the mercury has reached the juncture of the horizontal and vertical tubes, close *b* and allow the gas to remain in the Orsat tube for 3 minutes. Once more transfer the unabsorbed gas into the measuring-tube, taking care that none of the caustic potash solution comes with it (the latter should not quite reach the stopcock *b*). After bringing the gas to the atmospheric pressure, read the volume of the gas, the thermometer, and the barometer. As a rule, these readings of the barometer and thermometer remain constant; otherwise it is necessary to reduce the gas volumes in each case to 0° C and 760 mm pressure. The difference between the two volumes represents the amount of the carbonic acid gas. Remove the unabsorbed gas through *c* and repeat this whole operation of collecting the gas and absorbing the carbon dioxide until finally no more gas is given off from the liquid in *K*.

If it is desired to determine the amount of carbonate in a solid substance, a smaller decomposition flask should be used. Add the aluminum wire to the weighed substance and exhaust the apparatus by repeatedly lowering *M*, closing *a*, opening *c*, and then raising *M*. Finally allow the acid to act upon the substance and carry out the determination exactly as described above.

Computation of the Analysis. — Assume that from *a* grams of substance *V* milliliters of carbon dioxide were obtained, which was measured moist at $t°$ C and *B* millimeters pressure. First of all reduce the volume to 0° C and 760 mm pressure by the following formula:

$$V_0 = \frac{V(B - w) \cdot 273}{760\,(273 + t)}$$

In this formula, *w* represents the tension of aqueous vapor expressed in millimeters of mercury.

Since the density of carbon dioxide is 1.529* referred to air as unity and 1 ml of air at 0° and 760 mm pressure weighs 0.001293 g†, evidently

1 ml CO_2 weighs $0.001293 \times 1.529 = 0.001977$ g at 0° and 760 mm

* Cf. Lord Rayleigh, *Proc. Roy. Soc.*, **62**, 204 (1897); Guye and Pintza, *Mém. soc. phys. hist. nat. Genève* **35**, 569 (1908). According to these values the gram-molecular volume of carbon dioxide is 22.25 l.

† Landolt-Börnstein, *Phys. chem. Tabellen.*

and V_0 milliliters weigh $V \times 0.001977$ g. The percentage of CO_2 in the original substance is then

$$\frac{V_0 \times 0.1977}{a} = \text{per cent } CO_2$$

Remark. — The addition of aluminum is absolutely necessary. By boiling an acid solution, carbonic acid is not completely expelled; this is effected only when a different gas simultaneously passes through the solution. Formerly it was customary to pass air through the apparatus, but Pettersson accomplished the same purpose by generating hydrogen within the liquid itself.

(b) *Method of Lunge and Marchlewski**

Lunge and Marchlewski carry out the determination according to the same principle as that of the above process; *i.e.*, by simultaneously evolving hydrogen (aluminum and hydrochloric acid), measuring the gas, and absorbing the carbon dioxide by means of caustic potash in an Orsat tube.

The apparatus which they recommend is shown in Fig. 70, *b*. It consists of the 40-ml decomposition-flask N, the 140-ml measuring-tube A, the compensation tube C, and the leveling-tube B; the three last are connected together as shown in the figure.

In the case of all gas-volumetric methods, the volume of the measured gas must be reduced to 0° C and 760 mm pressure, which ordinarily requires a knowledge of the temperature and the barometric pressure. In this method the reduction is accomplished without paying any attention to the actual readings of the thermometer and barometer by means of the compensation tube C, which contains a known amount of air, viz., that amount of air which in a dry condition assumes a volume of 100 ml at 0° C and 760 mm pressure. If, therefore, this amount of air has a volume of V' at $t°$ and atmospheric pressure P' (with the mercury at the same level in B and C), we know that this volume of any gas would be equal to 100 ml at 0° C and 760 mm pressure. By raising the leveling-tube B so high that V' milliliters is compressed to 100 ml, we have accomplished the reduction in a mechanical way. If, however, there is a gas volume V'' in the measuring-tube A under the same pressure as that in the compensation tube (this is the case when the mercury level is the same in A and C), we can reduce this volume to the standard conditions by simply raising B until the volume of the gas in C is just 100 ml, taking care that the mercury remains at the same height in the tubes A and C. The volume of the gas V_0'' in A corresponds, therefore, to the volume of this gas at 0° C and 760 mm pressure, for it has been

* *Zeitschr. angew. Chem.*, **1891**, 229.

compressed to the same degree as the gas in C. This is apparent when we remember that at a constant temperature the product of the pressure into the volume remains a constant for any gas.

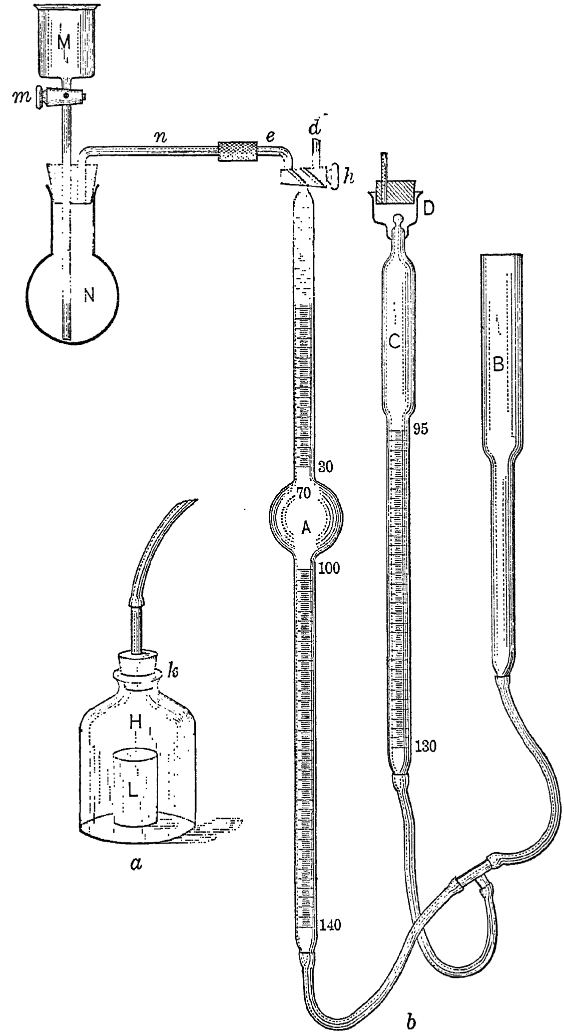


FIG. 70.

In the compensation tube we have the volume V' at atmospheric pressure P', and after compression the volume becomes $V_0' = 100$ ml and the pressure is P_0, from which it follows:

$$1.\quad V'P' = V_0'P_0$$

In the measuring-tube A, we have the volume V'' at the atmospheric pressure P', and after compression this volume becomes V_0'', and the pressure P_0, so that

$$2.\quad V'' \cdot P' = V_0'' P_0$$

By dividing equation 1 by equation 2 we have:

$$\frac{V' \cdot P'}{V'' \cdot P'} = \frac{V_0' \cdot P_0}{V_0'' \cdot P_0}$$

or

$$V' : V'' = V_0' : V_0''$$

and V_0'' is, therefore, the reduced gas volume that is desired.

Before using the apparatus for the determination, it is necessary to fill the compensation tube with the correct amount of air; this is accomplished as follows:

First of all, calculate what would be the volume of 100 ml of dry air measured at 0° C and 760 mm pressure when measured moist at the temperature of the laboratory and the prevailing barometric pressure. To illustrate, assume $t = 17.5°$ C; $B = 731$ mm; $w = 14.9$ (tension of aqueous vapor); then

$$\frac{100 \times 760 \times 290.5}{\quad} = 112.9 \text{ ml}$$

In such a case introduce 112.9 ml of air into the tube C by removing the stopper and lowering the leveling-tube until the mercury in the compensation tube stands at exactly 112.9 ml. Add a drop of water by a pipet, immediately stopper the tube and make an air-tight seal by covering the tube with mercury. Then press down a rubber stopper containing a glass tube into D. After this the temperature and pressure may vary as much as it will; the reduced volume of the air in C will always be equal to 100 ml.

Procedure for the Analysis. — Weigh out about 0.08 g of aluminum wire, *i.e.*, enough to furnish approximately 100 ml of hydrogen, into the decomposition flask. Add a sufficient weight of the substance to be analyzed so that about 30 ml and no more of carbon dioxide will be generated, and connect the flask with the funnel tube M, and capillary n. Also make connection with the tube A after it has been completely filled with mercury by raising B. Exhaust the air from N by lowering B, opening h so that e is connected with A, then closing h by turning it 90°, and carefully raising B until the mercury stands at an equal height in A and B; after this turn h so that A is connected with the capillary d, and expel the air in A. After repeating this process 3 or 4 times until

finally only 2–3 cm of air remain in A, lower B, add the necessary volume of 3 N hydrochloric acid to M, carefully open h, then m until 10 ml of the acid have run into the flask N, when m is once more closed. The carbon dioxide evolution begins at once and the mercury level quickly falls in A. Heat the contents of the flask to boiling over a flame and maintain this temperature until all the aluminum has dissolved. During the whole operation the mercury level in B must be kept lower than that in A. In order to transfer the gas remaining in the flask N into the tube A, fill M with distilled water, slowly open m and allow the water to run into N until the stopcock h is reached, then immediately close h. Compress the gas by raising the tube B until the mercury stands at the same height in A and C and the level in the latter tube is exactly at the 100-ml mark. Read the volume of the gas. After this connect the capillary d with an Orsat tube filled with caustic potash (1:2) (Fig. 71), drive over the gas in A into the Orsat tube, allow to stand 3 minutes, and transfer the unabsorbed gas to A, where its volume at 0° C and 760 mm pressure is determined as before. The difference in the two readings represents the volume of the carbon dioxide, and the percentage can be computed according to the formula

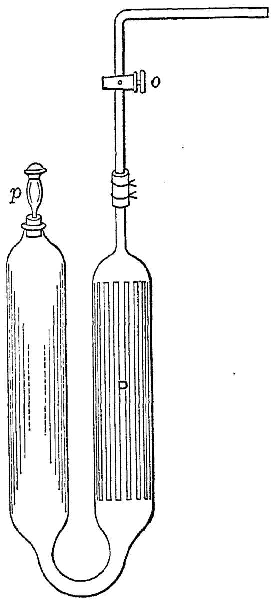


FIG. 71.

$$\text{Per cent } CO_2 \quad 0.1977 \cdot \frac{V}{a}$$

in which V is the amount of carbon dioxide absorbed in the Orsat tube and a represents the amount of substance taken for the analysis.

Remark. — This is the most exact of all methods for the determination of carbon dioxide in solid substances and is accomplished quickly. It is to be recommended where carbon dioxide determinations must be made daily, as, for example, in cement factories. It is necessary, however, to test the volume of the gas in the compensation tube from time to time to make sure that it really corresponds to 100 ml of air under the standard conditions of temperature and pressure.

For a single determination the author prefers to dispense with the compensation tube. In this case, however, the collected gas must be kept surrounded by water at a definite temperature, as in the Pettersson method, and the temperature and pressure must be observed. It is also well to make these readings in the above-

described procedure, to be sure that the volume in the compensation tube has remained constant.

(c) *Method of Lunge and Rittener**

In the decomposition flask K, Fig. 72, place 0.14–0.15 g of calcite, or a corresponding amount of any other carbonate, and fasten a small piece of aluminum wire, weighing about 0.015 g, to the neck of the flask. Allow about 1 ml of water to flow through the funnel, T, and then connect the capillary with the dry Bunte buret. Close the stopcock of the funnel T and open the two cocks of the Bunte buret. Connect the lower stopcock, h_1, with the suction pump, and produce a partial vacuum in the buret by letting the pump run 2–3 minutes, after which close h_1. Now from the funnel T, allow 2.5 N hydrochloric acid to flow upon the substance until it is decomposed completely; then heat the liquid to boiling,† taking care that no water gets into the buret. Add acid from T until the aluminum wire is reached and heat the flask again.

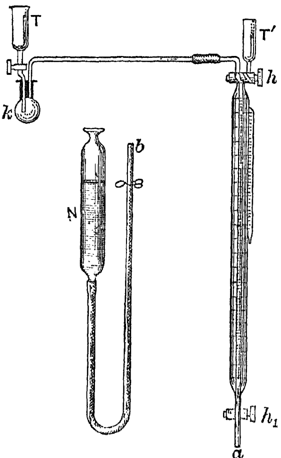


FIG. 72.

The hydrogen now evolved serves to expel the last traces of carbon dioxide from the flask. As soon as all the aluminum is dissolved, add hydrochloric acid through the funnel until the liquid reaches the stopcock h, which is then closed at once. Now connect the lower end, a, of the buret by rubber tubing with the leveling-tube N, which contains a saturated solution of common salt. By carefully opening the lower stopcock h_1 allow the salt solution to rise in the buret until the liquid there stands at the same height as in the leveling-tube, whereupon the stopcock h_1 is closed. Allow the apparatus to stand for 20–25 minutes so that the temperature of the gas will be that of the surroundings and then, by suitably raising or lowering the leveling-tube with h_1 open, read the buret, the thermometer, and the barometer. Fill the funnel T' of the buret with strong potassium hydroxide solution (1:2) and produce a partial vacuum in the buret, by lowering the leveling-tube and opening the stopcock h_1.

Allow the caustic potash solution to run into the buret by opening

* *Z. angew. Chem.*, 1906, 1849.

† Carbonates, such as magnesite, dolomite, or siderite, are decomposed so slowly by cold, dilute acid that it may be added much more quickly than prescribed above.

the upper stopcock h, but closing it before the last few drops of liquid leave the funnel. Mix the contents of the buret by shaking. By repeating the operation it is easy to tell whether the absorption of carbon dioxide has been complete. Read the residual volume with the usual precautions and the difference between the two readings gives the volume of the carbon dioxide.*

Compute the weight of carbon dioxide exactly as described on p. 351, except that the vapor tension of the saturated salt solution only amounts to 80 per cent of the tension of pure water at the same temperature.

Example: Weight of substance $= a$	Temperature $= t°$
Volume of hydrogen + air + $CO_2 = V_1$	Barometer $= B$ mm
Hydrogen + air $= V_2$	Tension of aqueous vapor $= w$ mm
$CO_2 = V_1 - V_2$	Tension of salt solution $= 0.8w$ mm.

The volume reduced to 0° and 760 mm, is, therefore:

$$V_0 = \frac{(V_1 - V_2) \cdot (B - 0.8w)\ 273}{760\ (273 + t)}$$

and the percentage of CO_2 in the substance (see p. 352) is

$$\frac{V_0 \times 0.1977}{a} = \text{per cent } CO_2$$

For the determination of carbon dioxide in mineral waters this apparatus is not suited; for this purpose the author has modified the Pettersson apparatus as shown in Fig. 73.

(*d*) *The Modified Method of Pettersson*

For decomposition flasks, use 70–200 ml Erlenmeyers (according to the supposed amount of carbonic acid) and etch the exact capacity of each flask upon it. To determine this, provide each flask with a tightly fitting stopper of gray (not red) rubber containing one hole, through which the small tube R is introduced. Fuse together the bottom of R but near the bottom make a small hole.

Push the tube R into the stopper until the small opening can be seen just below the bottom of the rubber stopper, and press the stopper as far as possible into the Erlenmeyer flask full of water. By this means some of the water passes from the flask into the tube R. Then raise the latter as is shown in Fig. 73, b; in this way an air-tight seal is made.

Remove the water in R by filter paper, and weigh the flask and contents to the nearest centigram. By deducting from this the weight of the empty flask together with the rubber stopper and R, the weight

* This is true if the temperature and pressure are the same as before the absorption of the CO_2. If not, both volumes must be reduced to 0° and 760 mm pressure before the difference is found.

of the water, *i.e.*, the volume of the flask, is obtained. By means of a piece of gummed paper fastened to the flask, note the position of the lower edge of the rubber stopper. Empty the flask, dry, and cover the neck of the flask as well as the paper strip with a thin coating of wax. Along the edge of the paper where the bottom of the rubber stopper came on the flask, cut a sharp line in the wax by means of a knife and write the capacity upon the wax with a pointed file. Etch these lines upon the flask by exposing them to the action of hydrofluoric acid for 2 minutes. Wash off the excess of the acid, dry the flask, melt the wax, and wipe off with filter paper. The flask is now ready to be used for the analysis.

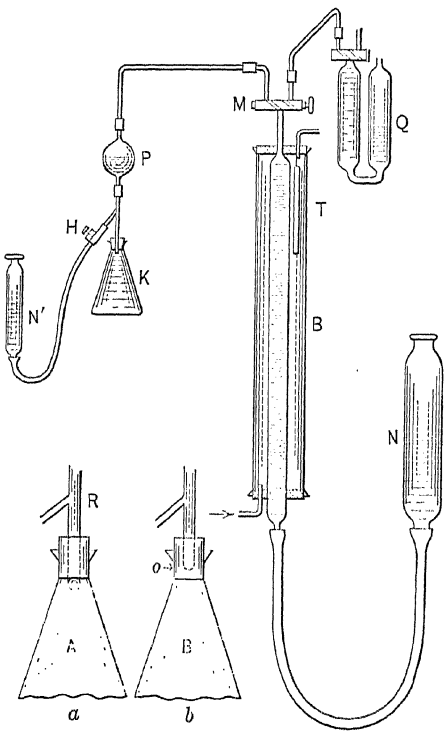


Fig. 73.

Place about 0.04 g of aluminum in the flask, and fill it by dipping into the spring. When this is not possible, place a piece of rubber tubing in the bottle containing the water to be analyzed, so that it reaches to the bottom, and siphon the water into the flask for 2–3 minutes. After this, close the filled flask by the rubber stopper with the tube *R* so that the bottom of the stopper reaches just to the mark again. Raise the tube *R* (Fig. 73, *b*) and wash out the spring-water within the tube by a stream of distilled water from a wash-bottle.* Then connect the flask with the bulb tube *P* (of about 40-ml capacity), which in turn is connected with the measuring-tube *B*. Place *B* in a condenser through which a stream of ordinary water constantly flows. Now connect the reservoir *N′* with the flask as shown

* With water containing much carbonic acid, cool the flask and its contents by ice in order to prevent it from breaking.

in the figure and close the screw-cock H. All rubber connections must be tightly fastened with wire.

Exhaust the bulb P by lowering N so that the air passes into B, whence it is driven into the Orsat tube O by turning the stopcock M and raising N. Repeat this operation 4 times. Then remove the air from the Orsat tube by suction through the right-hand capillary and change the stopcock to its original position as shown in the figure. Now press down the tube R into the flask so that the small opening reaches below the lower surface of the stopper.

Usually carbon dioxide is immediately evolved and the mercury in B at once begins to sink slowly. Hasten the evolution of the gas by gently heating the contents of the flask. As soon as the measuring-tube is almost entirely filled with gas, remove the flame, close M, and bring the contents of B under atmospheric pressure by raising N until the mercury in the two tubes is at the same height, and read its position in B. Take the temperature of the water surrounding B, read the barometer,* drive the gas over into the Orsat tube and allow it to remain there. Repeat this boiling, measuring, and driving over of the gas until only a slight gas evolution can be made to take place. In this way all the free carbon dioxide and a part of that present as bicarbonate is driven off, while that present as normal carbonate together with the rest of the bicarbonate remains in the flask; the liquid in the flask is usually turbid at this point owing to the precipitation of alkaline-earth carbonates. Now fill the reservoir N' with $4N$ hydrochloric acid (1:2) and remove the air from the rubber tubing by raising N' high and pinching the tubing with the fingers. Place the leveling-tube N in a low position, open H, and allow a little acid to run into K, after which H is again closed. As soon as the acid reaches the contents of K, a lively evolution of carbon dioxide ensues, which is afterward hastened by gentle warming. When the measuring-tube B is nearly filled, read its contents and drive over into the Orsat tube as before. Repeat the addition of the acid, etc., until finally the liquid in K clears up and the aluminum begins to evolve a steady stream of hydrogen, then heat the contents of the flask to boiling, but take care that none of the liquid in the flask is carried over with the escaping gas. As soon as the aluminum has completely dissolved, lower N, open H so that the flask is filled with the hydrochloric acid solution and the last portions of the gas are carried over into the measuring-tube B. As soon as the acid has reached the stopcock M, close it, and after reading the volume of the gas as before, transfer it to the Orsat tube. After remaining there 3 minutes

* If this analysis is made at the spring, it is necessary to have a sensitive aneroid barometer at hand.

bring back the unabsorbed gas to *B* and subtract its volume from the total amount of gas which has been expelled from the water that was analyzed. This difference represents the volume of the carbon dioxide gas. By correctly adjusting the current of water flowing through the condenser, the temperature at which the gas is measured will remain constant during the entire experiment.

From the volume of the absorbed carbon dioxide the percentage present is computed as was shown under the Pettersson method.

Determination of Carbonic Acid in the Air

See Part II, Acidimetry.

Determination of Carbonic Acid in the Presence of Other Volatile Substances

(a) Determination of Carbonic Acid in the Presence of Chlorine

If it is desired to determine the amount of carbonate present in commercial chloride of lime, chlorine will be evolved with the carbonic acid on treatment of the solid substance with hydrochloric acid, so that neither the direct nor the indirect method will give correct results. The determination can easily be effected by the following procedure:

Decompose the chloride of lime with hydrochloric acid and pass the evolved gases ($CO_2 + Cl_2$) into an ammoniacal solution containing calcium chloride.* After standing several hours in a warm place, quickly filter off the precipitate, wash with water, and determine the carbonate in the precipitated calcium carbonate by one of the usual methods.

Remark. — On conducting the mixture of chlorine and carbon dioxide into the ammoniacal solution of calcium chloride, the chlorine is changed into ammonium chloride with evolution of nitrogen, $8\,NH_3 + 3\,Cl_2 = 6\,NH_4Cl + N_2$, while the carbon dioxide is absorbed by the ammonia, forming ammonium carbonate, which is precipitated by the calcium chloride as calcium carbonate.

(b) Determination of Carbon Dioxide in the Presence of Alkali Sulfides, Sulfites, or Thiosulfates

Treat the solution to be analyzed with an excess of a solution of hydrogen peroxide containing potassium hydroxide, but free from carbonate. Boil to destroy the excess of the hydrogen peroxide, concentrate, and determine the carbonate preferably by the Fresenius-Classen method (p. 346).

* Dissolve 50 g of crystallized calcium chloride in 250 ml of water, add 500 ml of concentrated ammonia water, and allow the mixture to stand at least 4 weeks before using.

DETERMINATION OF CARBON

(1) *In Iron and Steel.*
(2) *In Organic Compounds.*

Carbon occurs in iron and steel as carbide, as a solid solution of carbide in iron, as graphite, and as temper carbon. Iron carbide, Fe_3C, is often called cementite. The properties of iron and steel depend not only upon the chemical composition of the material but also upon the treatment which has been given to it. Thus a steel with a given percentage of carbon may be very hard if it has been cooled quickly from say 1000°, or it may be much softer if it has been annealed. By polishing a piece of metal and etching the surface, it is possible to estimate by microscopical examination the percentage of carbon present, the heat treatment which has been given to the specimen, and whether the material is homogeneous. In testing steel and other alloys the work of the chemist should go hand in hand with that of the metallographer as either is likely to be led astray without the other.

In the chemical analysis of iron and steel the total carbon is usually obtained by combustion. In this country, this is usually done in the dry way with an electric furnace. In some parts of Europe a wet combustion, or oxidation by a mixture of chromic and sulfuric acids, is preferred. For a long time it was considered desirable to remove the iron by volatilization in a stream of chlorine (Wöhler) or by treating the metal with a solution of double chloride of copper and potassium (Berzelius-Richter), but at a temperature of 1100° it is possible to get complete oxidation of the sample without removing the iron, and the procedure is thus shortened.

The combined carbon is sometimes determined quickly by matching the color of the solution obtained by dissolving the steel in nitric acid, but the color is not strictly proportional to the carbon content and a hardened steel gives a different color from that given by an annealed steel with the same carbon content. If speed is required, it is possible to determine carbon by combustion in less than 10 minutes, so that there is no longer any excuse for carrying out the colorimetric determination except in small steel works with limited laboratory equipment.

(*a*) Determination of Total Carbon by Direct Combustion in Oxygen

Combustion tube and furnace. — The combustion should take place in a platinum, glazed porcelain, or silica combustion tube, which is so arranged that no compounds of carbon other than those obtained from the burning sample can possibly contaminate the current of gases flowing through it. The temperature of the portion of the tube occupied

by the sample should be maintained between 1050 and 1100° and the furnace should preferably be of the electric resistance type (Fig. 74).

Boats and lining. — Platinum, nickel, alundum, or clay boats may be used (Fig. 75), provided that the nickel, alundum, and clay boats are first proved to give no blank or a constant one of not over 0.0005 g. The lining or bedding material for the sample may be alundum, chrome brick, emery, or sand, provided the combined blank of boat and lining is

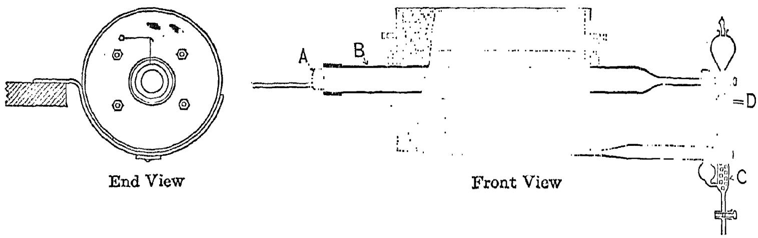


FIG. 74.

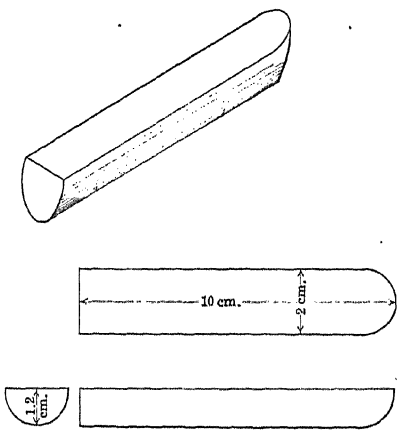


FIG. 75.

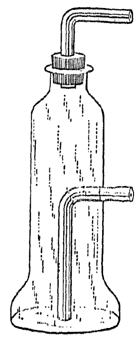


FIG. 76.

constant and not over 0.0005 g. To prevent injuring the combustion tube a shield of pure sheet nickel should encase the boat when in the tube.

Absorption tubes. — The glass absorption tube (Fig. 76) should be filled with soda-lime with phosphorus pentoxide on top or with ascarite (asbestos impregnated with anhydrous $NaOH$), using a plug of cotton at the top and bottom to prevent any loss of dust while the gas is passing through it. It should stand 20 minutes by the balance case before weighing. It should always be weighed filled with oxygen and against a

counterpoise. The absorption tube should be followed by a phosphorus pentoxide guard tube and a bubble tube containing a saturated solution of barium hydroxide as an "exhaustion indicator."

The combustion train recommended by Stetser and Norton* is shown in Fig. 77. *A* and *B* are 8-l aspirator bottles, *B* is filled with oxygen through the reducing valve *N*; the upper bottle is graduated for each 250 ml. The pressure of water from *A* forces oxygen into the furnace

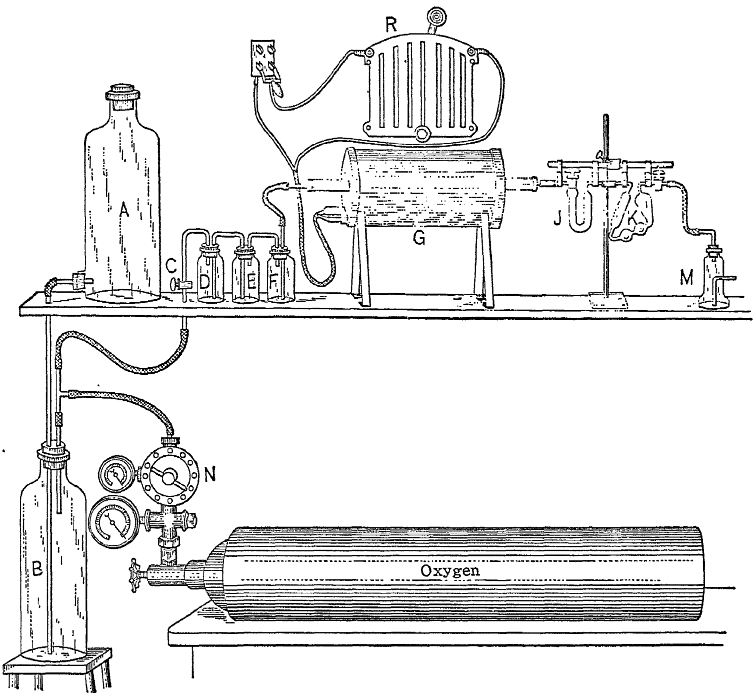


Fig. 77.

and the volume used is measured by the fall of water in *A*. *C* is a glass stopcock to be closed when filling *B* with oxygen. *D* is an empty safety bottle. Bottle *E* is one-third filled with concentrated sulfuric acid, and *F* contains ascarite. *J* contains 80-mesh zinc and *K* a little concentrated sulfuric acid. *M* (cf. Fig. 76) is the absorption bulb with ascarite which is a dehydrating agent itself so that no phosphorus pentoxide is required. Two of the ascarite bulbs should be filled and one used as a tare in weighing the other. A pair of the bulbs should accomplish about 140 combustions.

* *Iron Age,* **102,** No. 8.

The directions of Stetser and Norton emphasize the following precautions which are necessary for accurate work.

1. First test the apparatus to see if it is tight; with C open and K closed the pressure from A should not cause gas to bubble through E and K after a few minutes. Then close C and slowly open the stopcock on K. Fill B with water, open the gas regulator valve, and force the water from B into A. When A is full of water, close the regulator, and the train is ready for combustion.

2. For the combustion of 1 g of steel, about 300 ml of oxygen are required. Allow about 500 ml for the combustion and an equal volume to sweep out the carbon dioxide into the absorption tube. The gas will flow rapidly through the liquid in E when the sample starts to burn and will slacken when the combustion is finished. Place ignited asbestos in the front end of the tube.

3. A freshly filled absorption bulb should be run on the train for an hour and then weighed. Pass 2 l more of oxygen through the hot furnace and again weigh. The bulb should show less than 1 mg change in weight. It is well to check the efficiency of the apparatus by occasionally running a standard steel which can be obtained from the Bureau of Standards at Washington, D. C.

Procedure. — Connect the absorption tube M, with the cocks closed, to the train shown in Fig. 77, the guard tube, and the "exhaustion indicator." Place 1–3 g of weighed sample free from oil in a furrow in the bedding material in the boat so that the particles are in intimate contact. Introduce the boat into the hot combustion tube, close the tube, open the absorption tube, and turn on the current of oxygen. The rate of flow of the oxygen should be between 200 and 400 ml per minute and should continue for 10 minutes. Then close the absorption tube, turn off the oxygen, and place the absorption tube in the balance case. Remove the boat from the tube and examine the oxide of iron for complete fusion. If the fusion has not been complete repeat the determination.

The absorption tube and counterpoise, before being placed on the balance pan, should both be momentarily opened to the air to bring the pressure inside to that of the atmosphere. The increase in weight of the tube multiplied by 27.3 and divided by the weight of the sample in grams is equal to the percentage of carbon.

Note: In the case of alloy steels it is advisable to heat the chips to dull redness before turning on the oxygen and to employ a temperature of at least 1100° C.

Instead of absorbing the CO_2 formed by combustion and basing the analysis upon the gain in weight of the absorption tube a number of other methods have been devised. Often the CO_2 is absorbed in a solution of $Ba(OH)_2$. If a measured volume of barium hydroxide solution of known strength is used, the excess can be determined

by titration with acid until the solution is no longer alkaline to phenolphthalein; none of the $BaCO_3$ precipitate dissolves until after the solution is acid to phenolphthalein.

Methods of Cain and Maxwell*

Instead of absorbing the carbon dioxide in an absorption bulb containing soda-lime, ascarite, or strong potassium hydroxide solution (in the last case a Geissler bulb should be used) Cain and Maxwell recommend using a 10-bulb Meyer tube filled with barium hydroxide

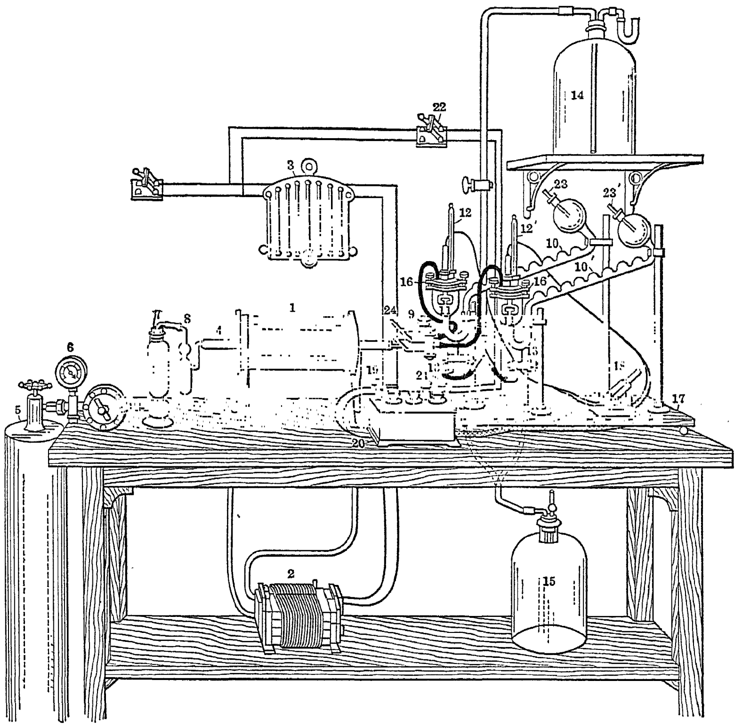


FIG. 78.

solution (25 g $Ba(OH)_2 \cdot 8H_2O$ per liter). Enough of the alkali should be used in an analysis to fill each small bulb of the absorption tube and half of the larger exit bulb.

During the combustion of the iron or steel, keep gas flowing through the Meyer bulbs. This requires a rapid stream of oxygen when the steel is burning. By placing a capillary tube in the rubber stopper at

* Bureau of Standards, *Technologic Paper No.* 33; *J. Ind. Eng. Chem.*, **10**, 520 (1918); **11**, 852 (1919).

the front end of the furnace, the rapid escape of gas from the furnace is hindered. This cuts down the flow of gas automatically when the combustion is over. At no time should more than 200 ml per minute of oxygen enter the combustion tube.

At the end of 5 minutes, the combustion should be complete. Disconnect the Meyer bulb, and the furnace is ready for another combustion.

Pour off the contents of the Meyer bulb into a Büchner funnel fitted to a suction flask and containing two 7-cm filter papers, one on top of the other. Wash out the tube 3 times with distilled water that has been boiled and cooled in a flask stoppered with a soda-lime tube in the stopper, so that no carbon dioxide can be absorbed from the air. Then wash the filter 4 times more, taking care that the top of the funnel is washed each time.

To the rinsed Meyer tube, add from a buret about 5 ml of 0.1 *N* hydrochloric acid more than is necessary to dissolve all of the barium carbonate precipitate. Transfer the acid from the Meyer tube to a wide-mouthed flask into which also place the filter papers containing a part of the precipitate. Rinse out the Meyer bulb with 2 portions of boiled water. It is then ready to be filled for another determination.

Heat the flask containing the acid until all of the barium carbonate has dissolved, cool and titrate with the 0.1 *N* NaOH using methyl orange as an indicator. (See Acidimetry.)

Cain and Maxwell have also worked out an electric resistance method which is still more rapid.* The apparatus is shown in Fig. 78.

The absorption apparatus is essentially a Meyer bulb capable of holding 200 ml of barium hydroxide solution when filled to the mark. The entrance bulb is modified so that a sensitive thermometer and a pair of platinized electrodes can be introduced. By means of a galvanometer and a specially constructed bridge, the electric resistance of the solution can be determined with the aid of an ordinary 60 or 25 cycle alternating current. A nomographic chart has been worked out so that the concentration of the barium hydroxide solution can be read in terms of percentage of carbon as soon as the electric resistance and temperature of the barium hydroxide are known. Thus the difference between the two readings, with a 2-g sample used for analysis, gives the percentage of carbon present. In carrying out a series of analyses at the Bureau of Standards the average time per analysis was 5 minutes.

* *J. Ind. Eng. Chem.*, **11**, 852, Bureau of Standards, *Technologic Paper, No.* 141. The necessary equipment can be obtained from the Arthur H. Thomas Co. of Philadelphia.

Determination of Graphite

Dissolve 1 g of cast iron in 50 ml of 6 N nitric acid in a 300-ml beaker and heat gently until there is no further evolution of gas. By this means the carbide carbon is dissolved while the graphite is not attacked. Filter the solution through an ignited asbestos filter and wash the residue with hot water, then with a hot solution of potassium hydroxide (*d.* 1.1), followed by hot water, dilute hydrochloric acid, and finally with hot water again until free from chloride. After drying at 110°, transfer the asbestos and graphite to a combustion tube and burn the carbon in a current of pure oxygen as described on p. 364.

(*b*) Determination of Carbon by Wet Combustion

The Chromic-Sulfuric Acid Method

In this method the borings, which should be as fine as possible and free from grease, are treated with a mixture of chromic and sulfuric acids and heated to boiling. Thereby, the iron goes into solution and the carbon is oxidized to carbon dioxide. In spite of a large excess of chromic acid, however, some carbon is likely to escape in the form of hydrocarbons and carbon monoxide, unless precautions are taken. To prevent such losses, Särnström* recommended leading the escaping vapors over copper oxide in a combustion tube,† 80 cm long, which is heated in a combustion furnace. Many experiments have shown that the method of Särnström gives exact results, although objection has been raised to the long combustion tube that is required.

Corleis has succeeded in simplifying the method by showing that a very short combustion tube, filled with copper oxide and heated by a single Bunsen flame, suffices if the sample is covered with a coating of copper during the treatment with chromic and sulfuric acids. In fact, the use of the combustion tube is unnecessary in an ordinary steel analysis, because only 2 per cent of the total amount of carbon present is lost in this case. In the analysis of ferromanganese and similar alloys, however, the use of the hot tube is to be recommended.

Ledebur‡ even found that the results obtained with irons rich in graphite were a little too high on account of the formation of some sulfur dioxide, but this error can be overcome by passing the gases through chromium trioxide just before they enter the combustion tube.

The apparatus required is shown in Fig. 79 and consists of a Corleis decomposition flask A with condenser.

The flask is connected, as shown in the drawing, on one side with a soda-lime

* Särnström, *Berg- und Hüttenm. Ztg.*, **1885**, 82, and Corleis, *Stahl u. Eisen*, **1894**, 581. With ferromanganese the loss amounts to 22.5 per cent of the total carbon, with steel 9 per cent. With ferromanganese the escaping gases contain, besides carbon dioxide and traces of heavy hydrocarbons, 18 per cent methane, 76 per cent hydrogen, 3 per cent oxygen, and 2 per cent carbon monoxide.

† A small tube of glass, quartz, or porcelain filled with copper oxide or platinized asbestos.

‡ *Leitfaden für Eisenhütten-Laborat.*

tower, *W*, at the bottom of which is placed a little concentrated caustic potash solution, and on the other side with a system of tubes. The tube *B* is about 10 cm long and contains chromium trioxide between 2 asbestos plugs. The tube *C* is 15 cm long, is made of difficultly fusible glass, and filled with granular cupric oxide. It is placed in a little box made of asbestos paper. Tubes *a*, *b*, and *c* are drying tubes, the first containing glass beads wet with concentrated sulfuric acid, the other two

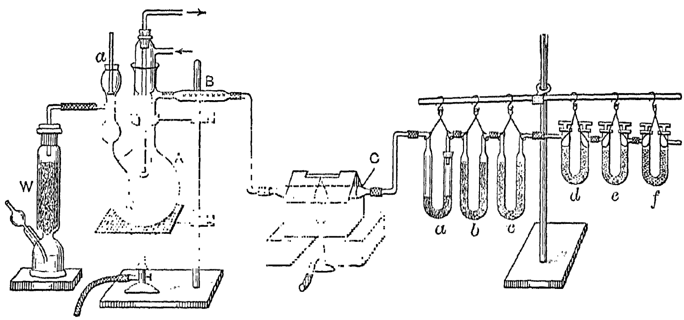


FIG. 79.

containing calcium chloride; *d* and *e* are glass-stoppered soda-lime tubes, the upper third of the right-hand arm of each containing calcium chloride. Instead of soda-lime, ascarite can be used (cf. p. 345). The tube *f* is a safety tube which is not weighed, but is used to avoid any chance of carbon dioxide or moisture entering the weighed tubes from the air.

Reagents. — 1. A saturated solution of commercial chromic acid, CrO_3, containing some sulfate. It is not advisable to use chemically pure chromic acid for this purpose, for the latter often contains organic substances.

2. A solution of copper sulfate made by dissolving 200 g of the salt in 1 l of water.

Procedure. — Remove the ground-glass stopper *a*, and through the opening pour 25 ml of chromic acid solution, 150 ml of copper sulfate solution, and 200 ml of concentrated sulfuric acid into the flask, *A*, and mix. Heat the mixture in the flask to boiling and keep at this temperature for 10 minutes. Then remove the flame and pass a current of air free from carbon dioxide through the apparatus for 10 minutes at the rate of about 3 bubbles per second. Connect the flask with the tube *B*, the red-hot copper oxide tube, and with the U-tubes,* while continuing the current of air for 5 minutes more. Remove the soda-lime tubes *d* and *e*, close, and allow to stand 10 minutes in the balance room. Open for a moment, quickly close, wipe dry with a piece of chamois skin, allow to stand 5 minutes in the balance-case, and then weigh.

* Corleis used phosphorus pentoxide for a drying agent, but calcium chloride is satisfactory, cf. p. 345.

By means of this preliminary boiling, traces of organic matter contained in the apparatus are removed.

After weighing the soda-lime tubes, connect them again with the apparatus, open the decomposition flask, and quickly drop in 0.5–5 g of the weighed substance, according to the amount of carbon present,* from a weighed glass-stoppered weighing tube, which is subsequently weighed again to determine the amount of sample. Immediately close the flask and heat the copper oxide tube to glowing, after which slowly heat the contents of the flask so that after from 15–20 minutes the liquid begins to boil. Keep the solution boiling for 1 or 2 hours while passing a slow current of air through the apparatus. Then remove the flame, and pass about 2 l more of air through the apparatus. Then remove the soda-lime tubes and weigh as before.

Since the use of the copper sulfate solution prevents the loss of more than about 2 per cent of the total amount of carbon present, it is evident that the combustion tube can be dispensed with for technical purposes.

(*c*) Combustion of Carbon in the Wet Way and Measuring the Volume of the Carbon Dioxide

This operation is best carried out by means of the Lunge-Marchlewski method: The apparatus necessary is shown in Fig. 70, p. 353. In this case, however, the decomposition flask is larger and there should be a ground-glass connection between the flask and a condenser. Furthermore, a funnel tube is fused into the neck of the flask, and runs along the side of the flask on the inside ending in a quite fine point near its bottom. The upper end of the condenser is connected with the measuring-tube by means of a capillary tube about 36 cm long, ground to fit the condenser tube.

Reagents. — 1. A saturated, neutral solution of copper sulfate.

2. A chromic acid solution (100 g CrO_3 in 100 ml of water).
3. Sulfuric acid, *d.* 1.65, and saturated with chromic acid.
4. Sulfuric acid, *d.* 1.71, also saturated with chromic acid.
5. Pure sulfuric acid, *d.* 1.10.
6. Commercial hydrogen peroxide solution.

Procedure. — The amount of iron or steel to be weighed out and the necessary quantities of the reagents are shown in the following table:

Per Cent C	Weigh in Grams	ml Copper Sulfate Solution	ml Chromic Acid Solution	ml Acid *d.* 1.65	ml Acid *d.* 1.71	ml Acid *d.* 1.10	ml H_2O_2
Over 1.5	0.4–0.5	5	5	135	....	30	1
0.8–1.5	1	10	10	130	....	25	2
0.5–0.8	2	20	20	130	....	5	2
0.25–0.5	3	50	45	....	75	5	2
Less than 0.25	5	50	50	....	70	5	2

* For cast iron 0.5 g suffices but for steel from 1–2 g and for wrought iron 5 g should be used.

Treat the substance with the copper sulfate solution in the decomposition flask at the ordinary temperature. Allow malleable iron to stand for at least 1 hour, but cast iron requires at least 6 hours. Connect the flask with the measuring-tube, which is filled with mercury, and exhaust the air in the flask as was described on p. 354. After this is accomplished, place the leveling-tube in a low position and add the proper amount of the chromic acid solution through the funnel, followed first by the proper amount of the stronger acid and then by that of the weaker acid, after which quickly close the stopcock in the funnel. The communication between the measuring-tube and the flask remains open. With the leveling-tube remaining in its low position heat the contents of the flask to gentle boiling, and boil for 1 hour. Then remove the flame. Now, in order to remove the last traces of carbon dioxide from the solution, add the prescribed amount of hydrogen peroxide to the contents of the flask and fill the flask with hot water until all the gas is driven over into the measuring-tube. Then close the stopcock b, reduce the gas to the volume corresponding to 0° C and 760 mm pressure as described on p. 352, and read this volume. Then drive over the gas into the Orsat tube containing potassium hydroxide solution and determine the volume of the unabsorbed gas as before. The difference between the two readings represents the amount of carbon dioxide measured under the standard conditions of temperature and pressure. This multiplied by the factor 0.0005392 gives the amount of carbon present.

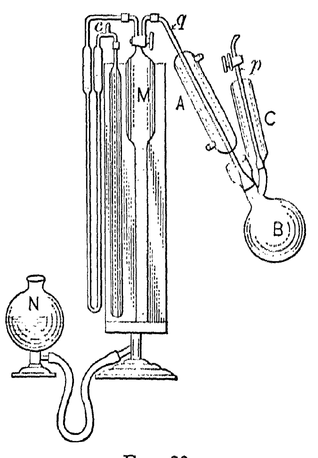


FIG. 80.

After the analysis has been completed, a blank determination must be made, using the same amounts of each reagent, in order to determine small amounts of organic matter which are invariably present in them. The amount of carbon dioxide found under these conditions must be subtracted from that obtained in the analysis proper.

*Method of Hempel**

Hempel objects to the above procedure on the ground that by dissolving the iron in the mixture of chromic and sulfuric acids some hydrocarbon is likely to escape oxidation. He found that by dissolving

* *Verhandlg. d. Vereins z. Beförd d. Gewerbefleisses*, 1893.

iron in chromic-sulfuric acid under diminished pressure in the presence of mercury all the carbon would be readily oxidized to its dioxide. Figure 80 represents the apparatus used.

Reagents Required

1. Chromic acid solution: 1000 g of chromic acid dissolved in 300 ml of water and 30 g of sulfuric acid, *d.* 1.704. The resulting solution has a density of 1.2.

2. Sulfuric acid: Mix 1000 ml of concentrated sulfuric acid with 500 ml of water and 10 g of chromic acid and heat for an hour in a large flask upon a sand-bath to destroy completely any dust, etc., that may be present. Then take away the flame and slowly conduct a current of air through the solution to remove any carbon dioxide that may have been formed. After cooling, dilute the solution with water until it has a density of 1.704.

Procedure. — Place about 0.5 g of the iron or steel in the decomposition flask *B*, add about 2.3 g of mercury by means of a small pipet, and connect the apparatus together as is shown in the drawing.

By raising the leveling-bulb *N*, fill the measuring-tube *M* with mercury, close the stopcock, and connect the apparatus at *p* with a suction-pump, by means of which exhaust the air in the flask *B* as completely as possible. To make sure that the ground-glass connection between the flask and the condenser is perfectly air-tight, pour a little water into the cup there. Into the funnel *C* place 30 ml of chromic acid solution, close the stopcock at *p*, and by carefully lifting the latter a little allow the chromic acid to run into the flask, and at once heat to boiling over a small flame. After boiling for half an hour, add 120 ml of sulfuric acid through *C*, open the stopcock at *M* for the first time, and boil the contents of the flask for half an hour longer. (At the start only carbon dioxide is generated, in proportion to the temperature of the solution, but toward the end of the operation there is a fairly lively evolution of oxygen.) Remove the flame, and carry over the gas in the flask into *M* by pouring water into *C* and lifting the tube *d* until the gas in the flask is entirely expelled. Read the total volume of the gas, and then absorb the carbon dioxide in a Hempel's potash pipet and determine the volume of the unabsorbed gas. The difference represents the amount of carbon dioxide formed by the oxidation. From this the amount of carbon present can be computed.

The measuring of the gas in this apparatus will be described more in detail in Part III, Gas Analysis.

Other methods for the determination of the volume of the carbon

dioxide formed from the carbon in iron or steel are those of J. Wiborgh,* Otto Pettersson, and August Smitt.†

For certain alloy steels and materials hard to oxidize such as ferro-silicon, ferro-chrome or tungsten steel, the following method is recommended:

Wöhler's Volatilization of Ferric Chloride Process‡

Principle. — The sample of iron or steel is heated in a stream of pure chlorine gas whereby iron, silicon, phosphorus, and sulfur are volatilized while the carbon remains behind in the presence of small amounts of non-volatile chlorides. The silicon present as silica, due to inclosed slag, is not affected by the treatment. The residue is filtered through asbestos, the chlorides washed out by water, and the carbon burned to dioxide either in the wet or in the dry way.

The principal requisite for the success of the process is *pure* chlorine. This must not contain oxygen, water, or carbon dioxide, because all these substances tend to convert a part of the carbon into carbon monoxide, whereby low results are obtained in the carbon determination.

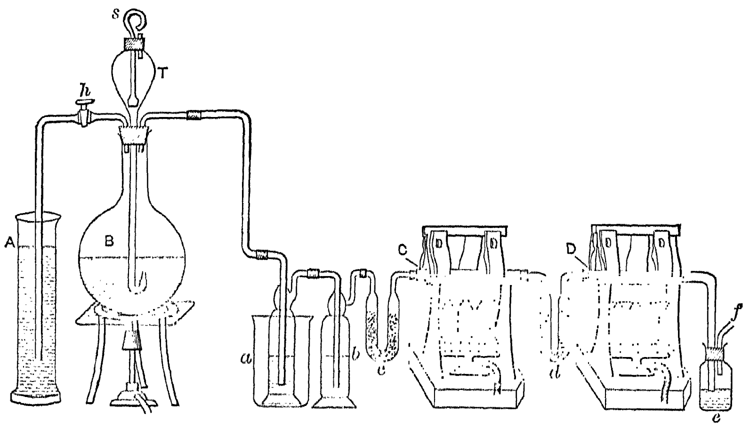


Fig. 81.

Procedure. — The specimen is subjected to the action of chlorine in an apparatus like that shown in Fig. 81.

B is the liter flask in which the chlorine is generated; it contains about 200 g of pyrolusite and 500 ml of concentrated hydrochloric acid. Heat the contents of the flask over a very low flame and in this way evolve a continuous stream of chlorine. When the current begins

* *Zeit. anal. Chem.*, **29**, 198 (1890).

† *Ibid.*, **32**, 385 (1893).

‡ *Z. anal. Chem.*, **8**, 401 (1869), cf. A. Ledebur, *Leitfaden für Eisenhütten Laboratorien.*

to slacken, add more hydrochloric acid through a Bulk's* dropping-funnel.† To regulate the current of gas, connect the flask with the right-angled tube, *h*, which is provided with a stopcock and leads to a cylinder, *A*, containing caustic soda solution. If the stream of chlorine becomes too strong, open the stopcock a little so that the excess of chlorine is absorbed by the sodium hydroxide. The chlorine is purified by means of the tubes *a*, *b*, *c*, *C*, and *d*; *a* contains water, *b* concentrated sulfuric acid, *c* glass beads, or pumice, moistened with sulfuric acid. *C* is a tube 40 cm long and 1 cm wide, made of difficultly fusible glass. It contains a layer, 15 cm long, of coarse charcoal which has previously been well ignited and cooled in a desiccator. The charcoal is placed in the tube between two loose plugs of ignited asbestos. Heat the tube to dark redness in a small combustion furnace. If the chlorine gas contains small amounts of oxygen (air) or carbon dioxide, these are changed, on coming in contact with the hot charcoal, to carbon monoxide, which is unaffected by the carbon in the iron or steel. Remove the last traces of moisture by passing the gas through the tube *d* containing glass beads moistened with concentrated sulfuric acid.

Next pass the chlorine into the combustion tube *D*. This is about 40 cm long by 1.5 cm wide, is bent into a right angle and leads into concentrated sulfuric acid in the flask *e*. The sulfuric acid serves as a seal and prevents air from getting into the tube.

Sprinkle the substance, which should be as fine as possible, as a thin layer‡ upon a previously ignited porcelain boat. Of ferro-chrome take about 0.5 g, and of ferro-silicon about 1 g. Shove the boat into the combustion tube and start the evolution of chlorine as described above. Do not heat the tube for about 20 minutes, when the air will have all been expelled; then begin heating very gradually, lighting the burners one at a time from right to left. The formation and volatilization of the ferric chloride takes place at a relatively low temperature.

As soon as no more brown vapors escape from the tube, gradually raise the temperature until the tube begins to get red; then allow the residue in the tube to cool in the stream of chlorine.

Remove the boat from the combustion tube, and, in the case of ferro-silicon, rinse the contents with cold water into a beaker. From the beaker wash the insoluble residue into an asbestos filter prepared as

* *Z. anal. Chem.*, **16**, 467 (1892).

† The flow of the acid is regulated by raising the tube *S*. Instead of *S* a glass rod covered with rubber tubing may be used.

‡ This is especially important with ferro-chrome, because otherwise the metal will become covered with a coating of non-volatile chromic chloride which prevents it from being acted upon by the chlorine.

follows: In the funnel *R*, Fig. 82, which is about 1 cm wide and 5 cm long, place a little glass wool, and upon this pour a suspension of ignited asbestos fibers in water until, with the aid of light suction, the filtrate comes through perfectly free from asbestos fibers. Wash the residue on such a filter with cold water until no chloride can be detected in the filtrate.

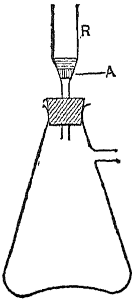


FIG. 82.

The carbonaceous residue can be oxidized in the apparatus shown in Fig. 79, p. 368, but in this case the flask *A* should contain 5 ml of a saturated, aqueous solution of chromic acid, and 60 ml of sulfuric acid, *d.* 1.71, which is likewise saturated with chromic acid.

In the analysis of ferro-chrome, there is always some insoluble chromic chloride in the boat which cannot be removed by washing. Therefore, heat the substance after the ignition in chlorine, in an atmosphere of hydrogen, whereby the insoluble chromic chloride is converted into soluble chromous chloride. The contents of the boat are then treated exactly as described above.

Determination of Carbon by the Berzelius-Richter Method

A number of methods have been proposed for dissolving away the iron and leaving the carbon behind in the form of an insoluble residue. For this purpose a solution of potassium-cupric chloride containing 300 g of the double salt ($2\,KCl \cdot CuCl_2 \cdot 2H_2O$) and 75 ml of concentrated hydrochloric acid to the liter has proved most satisfactory. Before using, filter the solution through ignited asbestos and preserve in a glass-stoppered bottle. The solution of the borings takes place very slowly unless the solution is stirred, which is best accomplished by means of a mechanical stirrer. Warming the solution also helps, but it should never be heated above 60°–70°. The following reactions take place:

$$Fe + CuCl_2 = FeCl_2 + Cu$$
$$Cu + CuCl_2 = Cu_2Cl_2$$

The presence of potassium chloride aids the solution of the copper, by forming a complex ion, $Cu_2Cl_4^{=}$.

The residue is filtered on an asbestos filter, dried, and burned in oxygen or in the Corleis flask. It may also be used for the determination of sulfur (see *Meinicke Method*, p. 325).

Determination of Carbon and Hydrogen in Organic Substances, according to Liebig

(Elementary Analysis)

Principle. — The organic substance is burned in air or in oxygen and the products of the combustion are passed over glowing copper oxide, which oxidizes all the carbon to carbon dioxide and the hydrogen to water. The water is collected in a weighed calcium chloride tube or sulfuric acid worm, the carbon dioxide in a weighed vessel which contains either caustic potash solution, soda-lime of 2 per cent moisture content and phosphorus pentoxide, or ascarite (asbestos impregnated with NaOH). Instead of the gas combustion furnace described here, many prefer to use an electric furnace.

The combustion is performed

(*a*) *In an open tube.*
(*b*) *In a closed tube.*

Combustion in an Open Tube

Most combustions take place in a tube open at both ends, and usually a gas-heated furnace and a glass tube are used. The progress of the combustion can be watched through the glass and a long horizontal column of copper oxide insures the complete combustion of the carbon. It is possible in many cases to use an electric furnace and carry out the combustion much more rapidly than heretofore. With the electric furnace, it is easier to get a constant temperature sufficient to burn the substance completely and with soda-lime of the best grade or with ascarite there is less danger of carbon results being too low. With the Geissler bulb and caustic potash solution, the rapid passage of gas causes volatilization of some of the water too fast to be absorbed by a short drying tube attached to the absorption bulb.

Pregl has shown that it is possible to simplify the process greatly by taking a smaller weight of substance and using a miniature apparatus. This requires a more sensitive balance than is ordinarily used. Pregl's argument that it is easier to get a perfect combustion with a small quantity of substance than with a larger quantity and that it is possible to realize the necessary refinement in weighing, is a perfectly sound one and many chemists are enthusiastic about the results obtained with the so-called *micro* apparatus. Pregl finds that the technique is easier for a beginner to master. For combustion in the old-fashioned way there are the following

Requirements. — (1) An open tube made of difficultly fusible glass which is from 12 to 15 mm wide. The length of the tube depends upon that of the combustion furnace; it must be 10 cm longer than the furnace. (2) 350 g of coarse and 50 g of fine copper oxide. (3) A drying apparatus (Fig. 83, on the left). (4) A cal-

cium chloride tube (Fig. 84). (5) A Geissler potash bulb (Fig. 85), or two soda-lime tubes or an ascarite bulb (Fig. 76, p. 362). (6) A screw-cock. (7) Dry rubber tubing. (8) Two plates of asbestos board to protect the rubber stoppers in the two ends of the tube from the heat of the furnace.

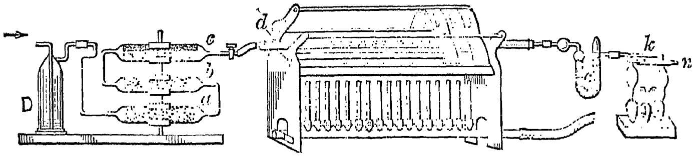


FIG. 83.

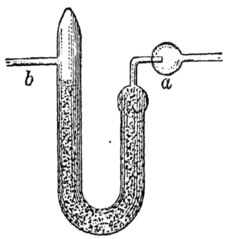


FIG. 84.

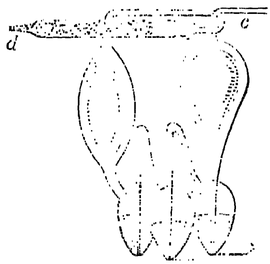


FIG. 85.

Procedure for the Combustion of Organic Substances Free from Nitrogen, Halogen, Sulfur, and Metals

Preparation and Combustion

1. *Fill the calcium chloride tube* (Fig. 84) from the left side, close with a plug of glass-wool, and fuse together the end of the tube, as shown in the figure.* It is more practical to use a calcium chloride tube fitted with ground-glass stoppers. After filling the tube, saturate with carbon dioxide (cf. p. 342, footnote).

Rub the outside of the tube with a piece of chamois skin, and stopper the two ends with short pieces of rubber tubing each containing a piece of stirring-rod. Allow the tube to stand in the balance case for 15 minutes and then weigh without the stoppers.

2. *Fill the Geissler bulb* (Fig. 85) with caustic potash solution (2 parts solid KOH in 3 parts of water) as follows: Replace the small drying tube *d* by a piece of rubber tubing, dip *c* into the solution of caustic potash, and fill the bulbs two-thirds full by sucking through the rubber tubing. Then clean the end of the tube *c* with a piece of filter paper, again connect the tube *d* (its right half is filled with soda-lime and the

* Or the tube is stoppered and an air-tight seal made by covering it neatly with aling-wax.

outer half with calcium chloride), close the two ends with pieces of rubber tubing each containing a piece of stirring-rod with rounded ends. Wipe the apparatus with chamois and weigh *without* the stoppers, taking the same precautions as with the weighing of the large calcium chloride tube.

3. *The drying apparatus* (Fig. 83, on the left), which serves to free the air and oxygen used for the combustion from carbon dioxide and water vapor, consists of a wash-bottle, *D*, containing concentrated caustic potash solution, the soda-lime tube *a*, and the 2 calcium chloride tubes *b* and *c*.

4. *The combustion tube* (Fig. 86), both ends of which are fire polished by heating in the blast lamp; after cooling, wash the tube, dry, and fill as follows: First place a short roll, *k*, of copper gauze at the right-

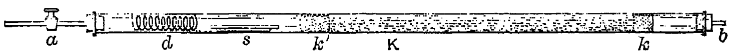


FIG. 86.

hand end of the tube so that 5–6 cm of the tube are left empty. This roll serves as a plug and must, therefore, fit tightly in the tube. Next add a layer of coarse copper oxide, *K*, about 45 cm long, and after this place another plug of copper gauze, *k'*. Finally insert another roll of copper gauze, *d*, about 10 cm long and large enough to fill the tube loosely, so that a space of about 10 cm is left on the right and about 5 cm on the left. Place the tube in the combustion furnace, so that about 5 cm extend beyond the furnace at each end, as shown in Fig. 83. Close the left end of the tube with a tightly fitting rubber stopper through which a glass tube passes, and connect with the drying apparatus by means of a short piece of rubber tubing. (The tube should be provided with a glass stopcock, which is shown in Fig. 86, *a*, but which is lacking in Fig. 83.) The right end of the tube is left open for the time being.

Pass a slow current of oxygen* through the apparatus and light the furnace. At first turn the flame low and heat the whole tube equally. Gradually raise the temperature, until, with the tiles covering the tube, the copper oxide is at a dull red heat.

Usually some water condenses in the right-hand end of the tube; expel this by carefully holding a hot tile under the tube. When all the water is removed, and the presence of oxygen can be detected at the

* The oxygen must be free from hydrogen. Commercial oxygen often contains the latter, in which case it is necessary to pass the gas through a "preheating" furnace before using it.

right end of the tube (by its igniting a glowing splinter), close this end of the tube with a rubber stopper connected to an open calcium chloride tube. Now turn down the burners and discontinue the oxygen current. Extinguish all the flames after some time except those under the right half of the tube.

While the tube is cooling, weigh the calcium chloride tube and the potash bulb (or soda-lime tubes), replacing the stoppers immediately after the weighing, and weigh 0.15–0.2 g of the substance into a porcelain boat.

If the substance is a difficultly volatile oil weigh it from a small glass tube open at one end. If it is readily volatile, blow a small bulb on a piece of narrow glass tubing and draw out the open end into a small capillary tube; weigh this, heat the bulb, and introduce the capillary into the liquid to be analyzed, so that the liquid rises in the bulb as it cools. Then turn the bulb so that the capillary lies in a horizontal position, heat slightly to expel a little liquid that adheres to the sides of the tube, melt the end together, and again weigh the tube. Take care that there is no liquid in the capillary. Everything is now ready for the combustion. Remove the stopper from the left (and now cold) end of the combustion tube, remove the long copper roll by means of a piece of wire with a hook in the end of it, place the boat with the substance in it in the tube and the copper roll right after it. Make connection with the drying apparatus on the left and with the absorption tubes on the right, as is shown in Fig. 83. If the substance is a liquid, place the bulb containing it so that its capillary is pointed towards the left, and with a volatile liquid break off the end of the capillary with a file just before introducing it into the combustion tube. Close the stopcock between the tube and the drying apparatus, connect the latter with an air-gasometer, and open wide the stopcock in the drying apparatus and that between the drying apparatus and the combustion tube just enough to permit 2, or at the most 3, bubbles of gas per second to pass through the apparatus. Light the two outer burners on the left and heat the copper oxide spiral *d* (the copper was changed to the oxide by the ignition in oxygen) just to redness. Gradually heat the tube from right to left, taking care that the gas evolution is never greater than 4 bubbles per second through the potash bulb; this can be easily regulated by means of the stopcock or by turning the gas-burners. When the contents of the entire tube have been brought to redness, with the tiles in place, and the boat is empty, the combustion is usually complete. It is well, however, to pass oxygen through the hot tube until the gas can be detected at the right-hand end of the combustion

train (a glowing splinter ignites at *n*).* Then turn down the flames and pass a current of air through the apparatus until the oxygen is completely expelled. A little water always collects in the front (right) end of the tube, and this must be driven over into the calcium chloride tube by holding a hot tile under it. Now remove the calcium chloride tube and the potash bulbs, wipe off with a piece of chamois skin, allow to stand in the balance room for 20 minutes, and weigh without the stoppers. The gain in weight represents the amount of water and carbon dioxide respectively, and from this the amount of hydrogen and carbon can be calculated.

Remark. — The combustion may be accomplished as described for the determination of carbon in steel but with the following precautions:

1. Place plugs of copper gauze and a layer of copper oxide in the front end of the furnace as described above, but use less copper oxide because of the shorter furnace. Before the combustion heat in oxygen to convert the copper to copper oxide, as described above, and to burn any dust in the tube.
2. Do not use more than about 0.1 g of substance and cover it with about 2 g of copper oxide powder. Use a slower stream of oxygen as only about 12 ml are required for complete combustion.
3. Have the combustion tube well cooled before introducing the boat with the substance and heat the front end of the tube first by moving the tube so that the part containing the boat is outside the furnace. When the front end of the tube is hot, place the tube in its normal position.
4. Use the absorption train as described above, without the zinc used in steel analysis, but substitute a Midvale or Fleming tube filled with good quality soda-lime or ascarite as described on p. 362.

Determination of Carbon and Hydrogen in Nitrogenous Organic Substances

By the combustion of many organic substances containing nitrogen, especially nitroso- and nitro-compounds, oxides of nitrogen are formed which are partly absorbed in the calcium chloride tube and partly in the potash bulb, so that if such substances were analyzed according to the previous process, both the carbon and hydrogen results would be too high. If, however, a reduced copper spiral is introduced in the front (right) end of the combustion tube, this serves to reduce the oxides of nitrogen to nitrogen itself, and, as nitrogen is not absorbed, correct results will be obtained.

Prepare the copper spiral by rolling together a piece of copper gauze about 10 cm wide, making it as large as will conveniently pass into the combustion tube. Heat the spiral till it glows by holding it in a

* To prevent moisture from getting into this tube from the air, it is well to connect it with an unweighed calcium chloride tube.

large gas flame, and while still hot drop it into a test-tube containing 1 or 2 ml of methyl alcohol. The alcohol quickly boils away, but some of it is oxidized to aldehyde by the hot copper oxide, which is reduced completely to bright metallic copper. Take out the spiral with a pair of crucible tongs and dry by quickly passing it through a flame a few times and while still warm introduce it into the front end of the combustion tube, which has been previously burned out as described in analysis.

To carry out the combustion, close the stopcock between the combustion tube and the drying apparatus (Fig. 83), insert the substance

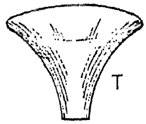
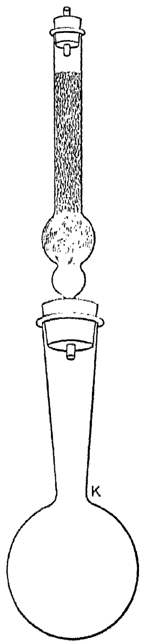


Fig. 87.



88.

Fig. 89.

into the tube, and first heat the copper oxide spiral at *d* and then the reduced spiral at the other end of the tube. Then beginning at *k* (Fig. 86), light one burner after another, until finally the entire contents of the tube are heated to dull redness and no more bubbles escape through the potash bulb. Now for the first time open the stopcock somewhat and pass oxygen through the tube until it can be detected at *n*, by a test with a glowing splinter. Then gradually turn down the

flames, replace the oxygen by air, and complete the analysis as in the previous case.

Substances hard to burn are treated somewhat differently. First of all fill the back end of the combustion tube (Fig. 83) with the aid of the funnel *T* (Fig. 87), with fine, granular, but not pulverized, copper oxide, and ignite this in a stream of oxygen. Replace the oxygen by air and allow the tube to cool until it can be held in the hand. Next transfer the fine, granular copper oxide to the small flask *K*, Fig. 88, and close the flask by inserting a tinfoil-covered cork, fitted with a calcium chloride tube. While the copper oxide in the flask is becoming perfectly cold, weigh the substance to be analyzed into the glass-stoppered mixing tube *M*, Fig. 89. Transfer from one-sixth to one-fifth of the copper oxide in the flask to the mixing tube, stopper, and shake the contents well, whereby the substance becomes intimately mixed with the copper oxide to which it adheres. Transfer the mixture back to the combustion tube, and shake the mixing-tube repeatedly with small portions of the remaining copper oxide in the flask until finally it can be assumed that all the substance has been transferred to the combustion tube. Then carry out the combustion in the usual manner.*

Combustion of Organic Substances Containing Halogens

The analysis is conducted exactly the same as for nitrogenous substances, except instead of a reduced copper spiral one of silver is used to keep back any halogen. The silver spiral should not be heated to redness, but only to about 180–200°. If a silver spiral is not at hand, use a long copper spiral, its end reaching outside the furnace.

Combustion of Organic Substances Containing Sulfur

Sulfur compounds cannot be burned in a tube containing copper oxide, for the sulfur dioxide escapes and is partly absorbed by the water in the calcium chloride tube and partly in the potash bulb, so that absolutely worthless results are obtained. Instead of the long layer of copper oxide, use one of ignited lead chromate; this oxidizes the sulfur dioxide to sulfur trioxide, forming difficultly volatile lead sulfate which remains in the tube. When lead chromate is used, the combustion must take place at a lower temperature than with copper oxide, for the chromate melts easily, and by adhering to the glass is likely to cause the tube to break.

* For another method of conducting a combustion in an open tube, consult M. Dennstedt, *Z. anal. Chem.*, **40**, 611 (1903).

Combustion of Organic Substances Containing Metals

If the substance contains alkalies, alkaline earths, or cadmium, a part of the carbon will remain in the tube as carbonate. In this case mix the substance in the boat with a mixture of 10 parts of powdered lead chromate and 1 part of potassium chromate, and conduct the combustion as when sulfur is present.

Dumas' Method for Determining Nitrogen in Organic Substances

This determination should really be discussed under Part III, but it will be described here on account of its being an analysis by combustion.

Principle. — The substance is burned in a combustion tube, free from air, which contains copper oxide and copper spirals exactly as in the determination of the hydrogen and carbon in substances containing nitrogen, but in this case the volume of the nitrogen evolved is *measured.*

Procedure. — This determination may be carried out in either a closed or open tube.

(a) Determination in a Closed Tube

The necessary apparatus is shown in Fig. 90. The combustion tube is closed at one end and is about 75 cm long. It contains at *M* a layer

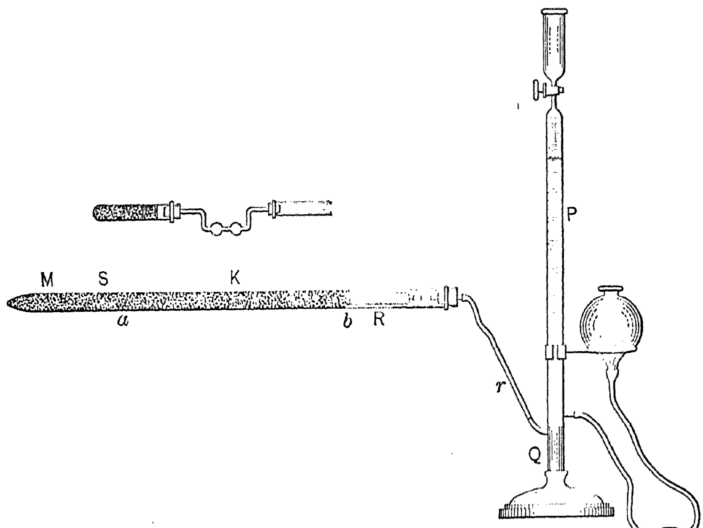


Fig. 90.

esi anese carbonate 15 cm long, in pieces about
of l by a loose plug of ignited asbestos and then

a 10-cm layer of coarse copper oxide, S. Add the substance at a in a boat and mix with powdered copper oxide by means of a spiral wire (cf. p. 381), then add a layer of coarse copper oxide* about 40 cm long and finally the reduced copper spiral (prepared as described on p. 380). Place the tube in a combustion furnace and connect as shown in the figure with an azotometer,† which contains mercury to a little above the lower end of r, and a liberal amount of caustic potash solution (300 g KOH dissolved in a liter of water).

Begin the analysis (with the leveling-bulb low and the stopcock of the azotometer open) by heating the left half of the magnesite layer, whereby the air in the tube is expelled by the carbon dioxide and passes through the azotometer. From time to time make a test to see whether all the air has been expelled. Raise the leveling-bulb, and close the stopcock with the azotometer tube completely filled. If all the air has been replaced by carbon dioxide gas, the bubbles of gas will all be absorbed by the caustic alkali. When this is the case put out the flame under M. Heat the tube first at R and light the burners one after another toward the left until about three-quarters of the layer of coarse copper oxide is heated to a dull redness. Then heat the tube at S and continue the process as in an ordinary combustion until the whole tube (with the exception of the part where the magnesite is found) is heated to a uniform temperature and finally no more nitrogen is evolved.

The heating must be accomplished so that there will be a slow but steady evolution of nitrogen. When the combustion is complete, heat the magnesite layer once more and expel all nitrogen remaining in the tube. As soon as the volume of the gas in the azotometer remains constant, measure the nitrogen.

For this purpose remove the azotometer together with the connecting piece of rubber tubing from the combustion tube and close the tubing by means of a pinchcock. Set the apparatus aside for at least 30 minutes at a place where a uniform temperature prevails, then raise the leveling-tube until the solution in it stands at exactly the same height as that in the tube. Read the volume of nitrogen, the thermometer, and the barometer.

The weight of the nitrogen present is computed as follows:

Assume a grams of the substance used for the analysis and V milliliters of nitrogen obtained at $t°$ and B millimeters barometric pressure. In order to obtain the weight of the nitrogen, its volume must be first

* The copper oxide must be previously ignited, as described on p. 381.

† H. Schiff, *Ber.*, **13**, 885.

reduced to 0° and 760 mm pressure. If the gas had been measured over pure water the formula

$$V_0 = \frac{V(B_0 - w) \cdot 273}{760\ (273 + t)}$$

would hold in which B_0 represents the observed barometer reading reduced to a temperature of 0° and w is the tension of water vapor measured in millimeters of mercury. The nitrogen, however, was not measured over pure water but over a solution of potassium hydroxide, and the vapor tension of this solution is less than that of pure water. In fact, with potassium hydroxide of the concentration used, the diminution of the vapor tension as compared with pure water almost exactly compensates the correction which would be applied in reducing the barometer reading to 0°. Consequently the following formula holds with sufficient accuracy:

$$V_0 = \frac{V(B - w) \cdot 273}{760\ (273 + t)}$$

As 1 ml of nitrogen at 0° and 760 mm has been found to weigh 0.0012506 g,* then V_0 milliliters of nitrogen will weigh

$$0.0012506 \times V_0 \text{ g}$$

and the substance contains $\frac{0.12506 \cdot V_0}{a}$ per cent of nitrogen.

If the value of V_0 is inserted in this last equation, and the constant values are united, it becomes

$$x = 0.04493 \frac{V(B - w)}{(273 + t) \cdot a} = \text{per cent N}$$

(b) Determination of Nitrogen in an Open Tube

The determination is carried out in practically the same way as before, except that the carbon dioxide is generated outside of the tube. If the combustion tube of Fig. 90 is imagined cut off at M and connected by means of the two-bulbed tube with a long test-tube, as shown in the upper part of the figure, the apparatus necessary for this determination will be seen.

The long test-tube contains sodium bicarbonate, and it is covered with a piece of copper gauze in order that it may be heated more uniformly.

At S is a long copper oxide spiral, this is followed by a copper boat containing the substance mixed with powdered copper oxide, then the

* Cf. Nitrogen under Gas Analysis.

long layer of coarse copper oxide, and finally the reduced copper spiral. After the connection with the azotometer has been made, heat the tube containing the sodium bicarbonate and remove the air from the combustion tube by means of the carbon dioxide evolved. The greater part of the water that is simultaneously set free collects in the two-bulbed tube. Otherwise the procedure is exactly the same as before.

Remark. — The advantage of this method over the former lies in the fact that the combustion tube can be used for a large number of nitrogen determinations without refilling it each time.

With difficultly combustible substances the author prefers to work with the closed tube, for in this way it is possible to get a very intimate mixture of the substance with the powdered copper oxide.

OXALIC ACID, $H_2C_2O_4 \cdot 2H_2O$. Mol. Wt. 126.05

Forms: Calcium Oxide, CaO, and Carbon Dioxide, CO_2

Determination as Calcium Oxide

Treat the neutral solution of an alkali oxalate with a few drops of acetic acid, heat to boiling, and precipitate with boiling calcium chloride solution. After standing 12 hours filter off the precipitate, wash with hot water, ignite wet in a platinum crucible, (p. 38) and from the weight of the calcium oxide calculate the amount of oxalic acid as follows:

Let a = weight of substance, p the weight of CaO from the CaC_2O_4 precipitate; then $\frac{224.6\,p}{a}$ = per cent $H_2C_2O_4 \cdot 2H_2O$.

Determination as Carbon Dioxide

Principle. — The method is based upon the fact that oxalic acid on being heated with manganese dioxide and dilute sulfuric acid is oxidized quantitatively to carbon dioxide:

$$H_2C_2O_4 + MnO_2 + H_2SO_4 = MnSO_4 + 2\,H_2O + 2\,CO_2$$

Procedure. — Treat a weighed amount of the oxalate with one and a half times as much manganese dioxide (free from carbonate) either in the apparatus shown on p. 342 (Fig. 67), or in that of Fresenius-Classen (Fig. 68, p. 345). The procedure is exactly the same as was described for the determination of carbon dioxide. If p grams of carbon dioxide were found, this corresponds to

$$p \cdot 1.431 = \text{grams oxalic acid, } H_2C_2O_4 \cdot 2H_2O$$

Remark. — Both methods give good results, but oxalic acid can be much more conveniently determined by a volumetric process (see Part II, Volumetric Analysis).

BORIC ACID, H_3BO_3. Mol. Wt. 61.84

Determination as Boron Trioxide, B_2O_3, by the Method of Rosenbladt-Gooch*

Principle. — Alkali and alkaline-earth borates, on being distilled with absolute methyl alcohol (free from acetone) and acetic acid, give up all their boron in the form of methyl borate, a liquid which boils at 65°. If the methyl borate is brought into contact with a weighed amount of lime in the presence of water, it is completely saponified:

$$B(OCH_3)_3 + 3\ H_2O = 3\ CH_3OH + B(OH)_3$$

The boric acid set free combines with the lime to form calcium borate. If the paste of water and lime is evaporated to dryness, the gain in weight, therefore, represents the amount of B_2O_3.

Procedure. — Ignite about 1 g of the purest lime† obtainable to constant weight over the blast lamp, and transfer as much of it as possible to the dry Erlenmeyer flask (Fig. 91) which serves as a receiver. Place the crucible, with some of the lime adhering to it, in a desiccator and set aside for the present.

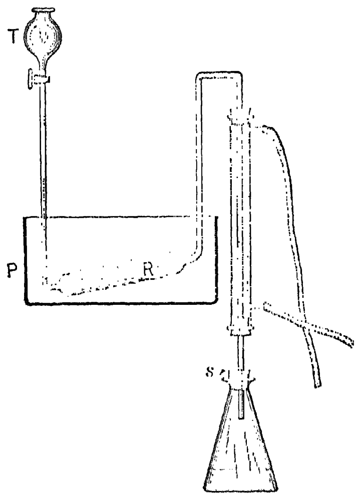


FIG. 91.

Slake the lime in the flask by carefully adding about 10 ml of water. Connect the flask with the distillation flask as shown in the figure.‡

Treat the aqueous solution of the alkali borate (containing not more than 0.2 g B_2O_3) with a few drops of either litmus or lacmoid solution, and add hydrochloric acid drop by drop until the solution turns red. Then add 1 drop of dilute sodium hydroxide and a few drops of acetic acid.§ Add the faintly acid solution by means of the funnel *T* to the

* *Z. anal. Chem.*, **27**, 18, 364 (1887).

† Instead of lime, Gooch and Jones use 4–7 g of sodium tungstate fused with about 0.5 g WO_3 in a platinum crucible to expel any carbonic acid. The fused mass is cooled and weighed.

‡ To permit the escape of air from the flask, make a cut in the side of the cork stopper, at *s*.

§ It is absolutely necessary to neutralize the greater part of the alkali with hydrochloric acid and then the last of it with acetic acid. If all the alkali were neutralized with acetic acid, little or none of the boric acid would pass over into the receiver during the subsequent distillation with alcohol.

pipet-shaped retort, *R*, of about 200-ml capacity. Rinse out the funnel 3 times with 3-ml portions of water and close the stopcock. Distil off the liquid by placing *R* in a paraffin bath at not over 140°, and collect the distillate in the Erlenmeyer flask containing the lime. When all the liquid has distilled over, lower the paraffin bath and, after *R* has cooled somewhat, add 10 ml of methyl alcohol (free from acetone) through the funnel and again distil off the liquid in *R*. Repeat this process 3 times. Then add 2–3 ml of water to the retort, a few drops of acetic acid until the liquid becomes distinctly red again,* and repeat the distillation with 10 ml of methyl alcohol 3 times more. At the end of this time all the boric acid will be found in the receiver. When the distillation is over, the retort should be removed from the paraffin bath by lowering the bath. If this is not done, the retort is likely to break when the paraffin solidifies. Shake the stoppered flask thoroughly and allow to stand for an hour or two to make sure that all the methyl borate is saponified. Then pour the contents of the receiver into a 200-ml platinum dish and evaporate on the water-bath to dryness at as low a temperature as possible. During this process the alcohol must not be allowed to boil under any circumstances. Then, in order to remove the small amount of lime that remained adhering to the sides of the flask, add a few drops of dilute nitric acid to the receiver, and, by carefully inclining the flask, wet its entire inner surface with the acid, after which wash the contents into the platinum dish and evaporate to dryness again. This time the water in the bath may boil, as there is now no danger of losing the boric acid, all the alcohol having been removed by the first evaporation. Gently ignite the residue in the dish over a small flame to destroy the calcium acetate that was formed by the excess of acetic acid added. Allow to cool and transfer by means of a little water to the crucible in which it was originally weighed. Dissolve the dark-colored lime remaining on the sides of the dish in a little nitric or acetic acid and wash into the crucible. Evaporate the contents of the crucible to dryness on the water-bath and, with the cover upon it, ignite the crucible at first gently and finally more strongly until a constant weight is obtained. The increase in weight represents the amount of B_2O_3.

Remark. — This method affords faultless results, even in the presence of considerable amounts of other salts. Free halogen hydride or sulfuric acid must not be present, for these acids form esters with the methyl alcohol and distil over with boric acid, with which they would be weighed. Instead of using lime in the receiver, the methyl borate can be distilled into a dilute solution of ammonium carbo-

* By the repeated distillation, the contents of the retort become alkaline, as shown by the blue color of the solution.

nate, and the latter evaporated with slaked lime in a platinum dish immediately after the distillation. The author, however, prefers the above method.

If one possesses a large platinum crucible (with a capacity of 80–100 ml), the first evaporation can take place in this and it is then advisable to place the crucible within a ring-shaped copper or tin tube through which steam passes (Fig. 25, p. 47). In this way the calcium acetate does not creep up over the sides of the dish, and there is no danger of any bumping.

Determination of Boric Acid in Silicates, Enamel, etc.

Fuse the finely powdered substance with 4 times as much sodium carbonate, extract the melt with water and evaporate the aqueous solution containing the boric acid* to a small volume, make acid with acetic acid, and, without regard to any separation of silica, transfer the solution to the Gooch retort and analyze as above directed.

Remark. — This determination can be performed in the presence of fluorine provided acetic and not nitric acid is used to set free the boric acid; but, for that matter, it is never advisable to use nitric acid and it is not permissible when chlorides are present.

Determination of Boric Acid in Mineral Waters

If the water contains considerable boric acid (0.1 g or more of B_2O_3 in a liter), evaporate a weighed amount (from 200 to 300 ml) to a small volume,† filter off the precipitated calcium and magnesium carbonates, concentrate the filtrate, make slightly acid with acetic acid, and analyze as described on p. 386.

If the water contains only a little boric acid, as is true in most cases, a large amount must be taken for the determination. Evaporate 10–15 l in a large porcelain dish to about 1 l,† filter off the deposited salts (these never contain any borate), wash thoroughly with hot water, and evaporate the filtrate and washings on the water-bath until a moist residue is obtained. If this residue does not amount to more than 5 or 6 g redissolve it in water, make acid with acetic acid, transfer to the Gooch retort, and distil as described on p. 386. Usually a larger residue is obtained, which can be conveniently analyzed directly; in this case the boric acid is extracted from it. For this purpose make the residue acid with a little hydrochloric acid, thoroughly stir with absolute alcohol, and by means of more of the latter transfer it to a flask, cork up, and allow to stand 12 hours with frequent shaking. The boric

* Sometimes the insoluble residue contains appreciable amounts of boric acid. In the method given under Volumetric Analysis, this fact will be taken into consideration.

† If the water reacts alkaline, evaporate it at once; otherwise add enough sodium carbonate solution to make it alkaline.

acid will then be found in the alcoholic solution. Filter off the residue, wash with 96 per cent alcohol, dilute largely with water, add 1 g of sodium hydroxide, distil off the alcohol (see Remark below), and evaporate the liquid until a moist residue is obtained. Make this again acid with hydrochloric acid and repeat the above extraction with alcohol, and subsequent distillation of the alcohol, after the addition of water and 1 g of sodium hydroxide. If the residue now obtained is not too large, ignite gently to destroy the organic matter; after extracting with water, filter off the carbonaceous residue and make the filtrate acid with hydrochloric acid. Then add sodium hydroxide till barely alkaline and just enough acetic acid to make the solution react acid again. Analyze the solution thus prepared as described on p. 386.

Remark. — Unless a large amount of water and the sodium hydroxide are added, some of the boric acid will be volatilized with the alcohol. It is always best to test the alcoholic distillate for boric acid as follows: extract a few pieces of turmeric root with alcohol, place 2–3 drops of the yellow solution in a porcelain dish, add the alcoholic solution to be tested for boric acid and a few drops of acetic acid. Dilute with water and evaporate to dryness on the water-bath. According to F. Henz, if as much as 0.001 mg of boric acid is present, a faint but distinct coloration will be evident, while the presence of 0.02 mg will cause a strong reddish brown coloration, which on being treated with sodium hydroxide is turned to the characteristic blue-black color.

If boric acid is found in the alcoholic distillate, it must be again treated with water and sodium hydroxide, and the alcohol once more distilled off.

MOLYBDIC ACID, H_2MoO_4. Mol. Wt. 162.02

The determination of molybdic acid has already been considered on p. 273.

TARTARIC ACID, $H_2C_4H_4O_6$. Mol. Wt. 150.05

The composition of free tartaric acid as well as that of the tartrates is determined by an elementary analysis; see pp. 375 *et seq.*

META- AND PYROPHOSPHORIC ACIDS

These acids are changed to phosphoric acid and determined as described on p. 390.

IODIC ACID, HIO_3. Mol. Wt. 175.93

Form: Silver Iodide, AgI

For the determination of iodic acid as silver iodide, make the solution of the alkali iodate acid with sulfuric acid, and add sulfurous acid until the solution, which at first becomes yellow on account of the sepa-

ration of iodine, is again colorless. After this add an excess of silver nitrate and a considerable amount of nitric acid. Heat the solution to boiling, and determine the precipitated silver iodide as described on p. 307.

It is not permissible to change the iodate to iodide by ignition, for the decomposition takes place at a temperature above that at which the iodide itself begins to volatilize. The transformation is, therefore, not quantitative. This is especially true of sodium iodate, which is only changed to iodide upon heating to a white heat. Potassium and silver iodates are much more readily decomposed, but even then some iodide is lost. Both iodic and periodic acids may be more accurately determined by a volumetric process (see Part II, Iodometry).

For the determination of the metal present in an iodate, first change it to the chloride by repeated evaporation with concentrated hydrochloric acid:

$$KIO_3 + 6\,HCl = KCl + 3\,H_2O + 2\,Cl_2 + ICl$$

GROUP IV

PHOSPHORIC, ARSENIC, ARSENIOUS, THIOSULFURIC, CHROMIC, VANADIC, AND PERIODIC ACIDS

PHOSPHORIC ACID, H_3PO_4. Mol. Wt. 98.05

Forms: Magnesium Pyrophosphate, $Mg_2P_2O_7$; Ammonium Phosphomolybdate, $(NH_4)_3PO_4 \cdot 12MoO_3$; Phosphomolybdic Anhydride, $P_2O_5 \cdot 24MoO_3$

1. Determination as Magnesium Pyrophosphate, according to B. Schmitz

Formerly it was the usual practice to precipitate phosphoric acid in the cold with "magnesia mixture" and ammonia, but according to the experiments of Neubauer* and of Gooch† it is evident that it is very difficult to obtain a pure precipitate of magnesium ammonium phosphate in this way; sometimes it is contaminated with $Mg_3(PO_4)_2$ and sometimes with $Mg(NH_4)(PO_4)_2$. If, however, the precipitation takes place in a hot solution, a very pure, coarsely crystalline precipitate of $Mg(NH_4)PO_4 \cdot 6H_2O$ is obtained.‡

Procedure. — To 50 ml of a neutral solution containing 0.1–0.5 g of P_2O_5 add a few drops of dilute hydrochloric acid, an excess of " mag-

* H. Neubauer, *Z. angew. Chem.*, **1896**, 439.

† F. A. Gooch, *Z. anorg. Chem.*, **20**, 135.

‡ B. Schmitz, *Z. anal. Chem.*, **65**, 46 (1924); K. K. Järvinen, *Z. anal. Chem.*, **43**, 279 (1904), **44**, 333 (1905); G. Jörgensen, *Z. anal. Chem.*, **45**, 278 (1906).

nesia mixture,"* 5 g of ammonium acetate, and a little phenolphthalein solution. Heat nearly to boiling, run in from a buret 1.5 N ammonia, while constantly stirring, until a turbidity forms. Stir till the precipitate is crystalline and then continue adding the ammonia until a red coloration is obtained from the indicator. Allow the solution to cool completely, add one-fifth of its volume of concentrated ammonia, and let stand at least 4 hours. Wash the precipitate 3 times by decantation with 1.5 N ammonia, then transfer to a filter, and wash free from chloride. Finally moisten the precipitate with a saturated solution of ammonium nitrate in 1.5 N ammonia, dry, ignite, and weigh as described on p. 81. It is best to use a filtering crucible and an electric oven.

If the weight of the precipitate is p, then the corresponding weights of H_3PO_4 and P_2O_5 are

$$\frac{2\,H_3PO_4 \cdot p}{Mg_2P_2O_7} = \text{weight } H_3PO_4 \quad \text{and} \quad \frac{P_2O_5 \cdot p}{Mg_2P_2O_7} = \text{weight } P_2O_5$$

The above method for the precipitation of phosphoric acid is not applicable when the substance contains alkaline earths or heavy metals. In such cases the phosphoric acid should be precipitated first as ammonium phosphomolybdate and the phosphoric acid in this precipitate determined by one of the following methods.

2. Determination of Phosphoric Acid as Magnesium Pyrophosphate after Previous Precipitation as Ammonium Phosphomolybdate

This method, first proposed by Sonnenschein, has experienced, in the course of time, a great many modifications.† It is always applicable when the phosphoric acid is present as orthophosphate.

Titanium, zirconium, quinquevalent vanadium, and quinquevalent arsenic interfere, all precipitating with the phosphorus. Titanium and quinquevalent vanadium also prevent complete precipitation. Cain and Tucker‡ have shown that the interference of vanadium can be prevented by reducing it to the quadrivalent condition and precipitating

* The "magnesia mixture" is prepared, according to Schmitz, by dissolving 55 g of magnesium chloride $MgCl_2 \cdot 6H_2O$ and 105 g of ammonium chloride in water, adding a little hydrochloric acid and diluting to a volume of 1 l. For 0.1 g of P_2O_5, use 6 ml of this solution.

† Cf. Woy, *Chem. Ztg.*, **21**, 442; Hundeshagen, *Z. anal. Chem.*, **28**, 164; Eggertz, J. pr. Chem. **79**, 406; v. Jüptner, *Oesterr. Z. Berg-Hüttenw.*, **1894**, 4711; McCandless and Burton, *Ind. Eng. Chem.*, **16**, 1267 (1924); McNabb, *J. Am. Chem. Soc.*, **50**, 300 (1928).

‡ *J. Ind. Eng. Chem.*, **5**, 647 (1913).

at 20° and by precipitating at this low temperature the interference of arsenic is overcome.

Principle. — If a solution containing phosphoric acid in the presence of ammonium nitrate and sufficient nitric acid is treated with an excess of ammonium molybdate and heated to 60–70° all the phosphoric acid is precipitated as yellow ammonium phosphomolybdate. When dried at room temperature over $CaCl_2 \cdot 2H_2O$, the precipitate corresponds to the formula — $(NH_4)_3PO_4 \cdot 12MoO_3 \cdot 3H_2O$ if it has been thoroughly washed with water or with potassium nitrate solution* and to $(NH_4)_3PO_4 \cdot 12MoO_3 \cdot HNO_3 \cdot 2H_2O$ when washed with dilute nitric acid. It always contains, when sufficient molybdic acid is present, 24 moles of MoO_3 to 1 mole of P_2O_5.

The precipitate is soluble in alkaline solutions and forms most readily when considerable free nitric acid is present; 1 g of P_2O_5 requires 11.6 g of HNO_3, but as much as 35.5 g of the acid does no harm.† The precipitate will dissolve somewhat if more nitric acid than the above quantity is used, but the addition of ammonium molybdate decreases the solubility of the precipitate in nitric acid; 1 g of ammonium molybdate makes 55.7 g of nitric acid inactive. The presence of ammonium nitrate not only facilitates the formation of the precipitate, but its presence is absolutely necessary, although about 5 per cent is sufficient.

In the United States, it is customary to use an *acid* solution of ammonium molybdate as reagent (see p. 394, footnote). This reagent contains the proper quantities of ammonium salt and nitric acid and is a sensitive precipitate for phosphoric acid. When this reagent is used, it is customary to make the solution nearly neutral and then add an excess of reagent.

Procedure. — To 50 ml of solution containing 0.1 g of P_2O_5 or less, carefully add 6 N ammonium hydroxide until the solution is neutral to litmus. Add a few drops of 6 N nitric acid, heat the solution to about 65°, and add 75 ml of ammonium molybdate reagent.‡ Keep the solution at this temperature for half an hour, filter, and wash once by decantation with an acid solution of ammonium nitrate§ and at least six times on the filter. When the washing is complete place the flask containing the bulk of the precipitate under the funnel and allow 6 N ammonium hydroxide solution to drop upon the upper edge of the filter from a buret, until enough has been added to dissolve all the precipitate on the filter paper and that in the flask. Rotate the contents of the flask from time to time and avoid using an unnecessary excess of ammonia. Wash the filter paper thoroughly with hot water. The volume should not exceed 100 ml at this point. Drop a piece of sensitive litmus paper into the solution and add 6 N hydrochloric acid, with constant rotation

* M. Ishibashi. *Mem. Coll. Sci.* A, **12**, 135 (1929).

† These figures are taken from experimental data furnished by Hundeshagen. They do not refer to the above formula of the yellow precipitate.

‡ See p. 394.

§ Mix 100 ml of 6 N ammonium hydroxide with 325 ml of 6 N nitric acid and dilute with 100 ml of water.

of the flask, until the litmus paper changes to a violet verging on the blue rather than the red. Add 10 ml of magnesia mixture* and heat almost to the boiling point. Add 2–3 drops of phenolphthalein indicator, and neutralize with 1.5 *N* ammonium hydroxide until the solution is colored pink by the indicator. Cool, add one-fifth of the solution's volume of concentrated ammonium hydroxide, and allow to stand for at least 4 hours. Filter, wash, ignite and weigh as directed on p. 391.

3. Direct Determination of Phosphoric Acid as Ammonium Phosphomolybdate (Finkener)†

The precipitate produced as described under 1 is heated until it becomes changed to $(NH_4)_3PO_4 \cdot 12MoO_3$. Theoretically this contains 3.784 per cent of P_2O_5, but better results are obtained if it is assumed to contain 3.753 per cent of P_2O_5.‡

Baxter§ recommends heating the precipitate to about 300° as does Ishibashi.|| The precipitate then contains 3.784 per cent P_2O_5 and corresponds to the formula $(NH_4)_3PO_4 \cdot 12MoO_3$. Baxter prepared the molybdate reagent as follows: Dissolve 150 g of commercial ammonium molybdate in 1 l of water and pour into an equal volume of 6 *N* nitric acid. Use 50 ml for 0.1 g of P_2O_5. Ishibashi used a 3.5 per cent solution of $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ in pure water. To a neutral solution of 6–70 mg of P_2O_5 he added twice the theoretical requirement of molybdate solution, 20 ml of 5 *N* ammonium nitrate solution and 20 ml of 5 *N* nitric acid making a total volume of about 100 ml. He heated with stirring at 60° for 5 minutes, allowed to stand 3 hours, filtered into a filtering crucible, washed with 2 per cent nitric acid, heated slowly to 250° and kept at 250°–300° for 30 minutes.

Procedure. — Precipitate the phosphoric acid with ammonium molybdate as directed on p. 392; filter the precipitate into a Gooch crucible, wash with ammonium nitrate solution until very little brown coloration is produced in the filtrate upon adding $K_4[Fe(CN)_6]$, and dry in a current of air at 160° in a Paul's drying-oven, until a constant weight is obtained. If the precipitate should become slightly greenish, add a small crystal of ammonium nitrate and one of ammonium carbonate and again heat the contents of the crucible, whereby the precipitate will at once assume a homogeneous yellow color.

Remark. — The results of Hundeshagen and Steffan show that this method gives very exact results. Steffan worked precisely according to the directions of Finkener, precipitating the phosphoric acid in the cold with a 33⅓ per cent solution of ammonium molybdate and filtering after standing 24 hours. It is, however, not necessary, as Hundeshagen has shown, to work with such a concentrated solution of ammonium molybdate; the precipitation from a hot solution with a 3 per cent molybdate solution yields just as accurate results and the solution does not have to stand so long

* See p. 391.

† *Ber.*, **11** (1878), 1640.

‡ Hundeshagen, *loc. cit.*

§ *Am. Chem. J.*, **28**, 298 (1902).

|| *Loc. cit.*

before filtering. Even when iron is present this method gives good results, so that it is to be recommended for the determination of phosphorus in iron and steel.

4. Determination of Phosphoric Acid as Phosphomolybdic Anhydride (Woy)

Gently ignite the precipitate, produced in the same way as before, until a greenish black residue remains of the composition $24\ MoO_3 \cdot P_2O_5$, with 3.94 per cent of P_2O_5. Perform the ignition as follows: Upon the bottom of a nickel crucible place a disk of ignited asbestos about 2 mm thick, or the porcelain plate of a Gooch crucible may be used. Upon this place the Gooch crucible containing the precipitate, cover with a watch glass and heat at first gently and finally until the bottom of the nickel crucible is at a dull red heat. When the precipitate has become of a homogeneous, bluish black color, allow to cool in a desiccator and weigh.

This method is rapid and gives good results in the presence of iron and aluminum.

Determination of Phosphorus in Iron, Steel, and Bronze*

Procedure. — **Cast Iron.** — Dissolve 1–3 g of sample in a covered casserole in 30 ml of 7.5 *N* nitric acid. When all the iron is in solution, add 10 ml of 6 *N* hydrochloric acid, evaporate to dryness, and bake on the hot plate for 15 minutes. Cool, drench the residue with concentrated hydrochloric acid, dilute to 50 ml, and heat until all the salts are in solution. Filter without delay, wash the residue with 0.6 *N* hydrochloric acid, and evaporate the filtrate to sirupy consistency. Meanwhile ignite the above residue in a platinum crucible, cool, and heat with 10 drops of concentrated hydrochloric acid and 2 ml of hydrofluoric acid. Evaporate just to dryness, add 5 ml of concentrated hydrochloric acid and add to the main solution that is being evaporated.

When the solution is of sirupy consistency, transfer to a 300-ml Erlenmeyer flask by alternate rinsing with 7.5 *N* nitric acid and hot water, using not more than 30 ml of the acid and 70 ml of the water. Heat to boiling and digest for 10 minutes.

Precipitation. — To the boiling solution, add 100 ml of ammonium molybdate solution†, shake 10 minutes and allow to stand at least 4 hours. If an appreciable amount of vanadium is present, carry out the

* G. E. F. Lundell, *Ind. Eng. Chem.*, **15**, 171 (1923).

† Stir 100 g of pure MoO_3 into 400 ml of cold distilled water and add 80 ml of concentrated ammonium hydroxide. Filter and pour while stirring into 1 l of 6 *N* nitric acid. Add 50 mg of microcosmic salt and allow to stand 24 hours before using. Do not prepare more than a week's supply of the acid reagent at a time.

precipitation at 20° in a solution which has just been treated with 2–3 ml of 10 per cent ferrous sulfate solution and a few drops of sulfurous acid to reduce quinquevalent vanadium. Decant off the solution through a filter, keeping as much of the precipitate as possible back in the flask, and wash with not more than 50 ml of cold 1 per cent nitric acid. Dissolve the precipitate in 24 ml of 6 N ammonium hydroxide to which 2 g of citric acid has been added. Pour the solvent through the filter that contained some of the phosphomolybdate and catch the solution in the flask containing the bulk of the precipitate. Finally wash the filter several times with 0.6 N hydrochloric acid. If the ammoniacal filtrate is not clear, heat it to boiling, filter through the same filter, and wash with hot water. In this case, and whenever appreciable quantities of elements like titanium, zirconium, and tin are present, preserve this filter paper and treat it together with the filter referred to in the following directions.

Make the ammoniacal solution acid with hydrochloric acid, add 20 ml of magnesia mixture and precipitate magnesium ammonium phosphate as described on p. 392. Allow the precipitate to stand 4 hours. Filter, keeping the precipitate back in the flask as much as possible. Dissolve the precipitate on the filter with 28 ml of 6 N hydrochloric acid, catching the solution in the flask containing the bulk of the precipitate. Wash the filter thoroughly with 0.6 N hydrochloric acid. If titanium, zirconium or tin is present, ignite this filter and the one previously set aside, in a platinum crucible, fuse with a little sodium carbonate extract with water, and add the aqueous extract to the hydrochloric acid solution of the first magnesium ammonium phosphate precipitate.

Transfer the solution to a 200-ml beaker. If considerable arsenic is present precipitate with hydrogen sulfide, washing the arsenic sulfide precipitate with dilute hydrochloric acid saturated with hydrogen sulfide. Boil off the excess of hydrogen sulfide and reduce to 50–75 ml. If only a little arsenic is present, add 0.6–1 g of ammonium bromide and evaporate the solution to a volume of 5–10 ml; the arsenic will volatilize as arsenic trichloride.

To the solution free from arsenic, and at a volume of 50–75 ml, add 0.1–0.2 g of citric acid and 2–3 ml of magnesia mixture, and again precipitate magnesium ammonium phosphate.

Ignite and weigh the magnesium pyrophosphate as described on p. 391.

Plain Carbon Steel. — Dissolve 1–3 g in 30 ml of 7.5 N nitric acid. When all the steel has dissolved, boil and slowly add a saturated solution of potassium permanganate until oxides of manganese are precipitated. Clear the solution by cautious addition of 10 per cent

ferrous sulfate solution, boil gently for 10 minutes, and treat with ammonium molybdate as above described.

Alloy Steels. — Treat *chromium* steels in the same way, but if any residue is obtained on dissolving in nitric acid, continue heating until it dissolves, adding sulfuric acid if necessary. Treat a high *silicon* steel like cast iron. If *titanium* or *zirconium* is present to any extent, a phosphate may precipitate during the boiling prescribed for plain carbon steels. Filter off the precipitate, fuse the residue with sodium carbonate and add the aqueous extract of the melt to the main solution. *Tungsten* steel does not dissolve in nitric acid. Dissolve 1–3 g in a mixture of 20 ml concentrated nitric acid and 60 ml of concentrated [illegible]hloric acid in a covered casserole. Heat gently and evaporate [illegible]ess. Remove the cover glass and bake till all the acid is expelled. [illegible]ool, and add 30 ml of concentrated hydrochloric acid. Heat until the iron all dissolves, dilute to 100 ml, filter, and wash the residue of tungstic acid with N hydrochloric acid. Evaporate the filtrate to a sirup and meanwhile dissolve the tungstic acid in hot $2N$ ammonium hydroxide, finally washing the paper with dilute hydrochloric acid. Make the ammoniacal solution faintly acid, add 1 g of alum and then add ammonium hydroxide in slight excess. Filter off the aluminum hydroxide and phosphate, dissolve in hot hydrochloric acid and add the solution to the main solution which is being evaporated. Dilute the sirup as described for the analysis of cast iron.

Bronze. — See p. 233.

The Lead Molybdate Method

Ibbotson* prefers to base the phosphorus determination upon the weight of $PbMoO_4$ that can be obtained from the $(NH_4)_3PO_4\cdot12MoO_3$ precipitate. The $PbMoO_4$ weighs 142 times as much as the phosphorus originally present. For [illegible] small quantities of phosphorus this is one of the quickest and most [illegible]hods.

[illegible] the ammonium phosphomolybdate precipitate (see p. 392) and wash it on a 9-cm ashless filter paper with cold 1 per cent nitric acid (1 ml concentrated acid and 100 ml water) at least 10 times. Dissolve the precipitate by pouring 4 ml of concentrated NH_4OH on the filter. Catch the solution in the flask used for the precipitation, wash the paper once with hot water, and again pour this solution through the filter, this time catching it in a 150-ml beaker. Wash the paper at least 6 times with a stream of hot water directed against the upper edge of the paper and then place the solution on a hot plate. Place beside it a 250-ml beaker containing a filtered solution of 10 g NH_4Cl and 12.5 g

* *Chemical Analysis of Steel Works' Materials.*

of ammonium acetate in 50 ml of water. When both solutions are at the boiling point, add, to the ammoniacal solution of the yellow precipitate, 10 ml of concentrated hydrochloric acid and 10 ml of 4 per cent lead acetate solution. At once pour this mixture into the hot solution of ammonium chloride and acetate, and wash out the beaker with hot water. Allow the precipitate to settle for a few minutes and then filter through a weighed Gooch crucible. Wash thoroughly with hot water until free from chloride, dry in the hot closet at 105°, and weigh. Or, if desired, finish the washing with alcohol and ether (cf. p. 81).

In this method of analysis, 12 $PbMoO_4$ are obtained for each P present. The weight of phosphorus, therefore, is found by the formula:

$$P = \text{Wt. ppt.} \times \frac{P}{12\ PbMoO_4} = \text{wt. ppt.} \times \frac{31.02}{4407} = \text{wt. ppt.} \times 0.00704$$

Determination of Phosphoric Acid in Silicates

In the analysis of silicates (see p. 433) the phosphoric acid is found in the precipitate produced by ammonia in the filtrate from the silica together with iron and aluminum hydroxides. It is analyzed according to p. 117.

Determination of Phosphoric Acid in Mineral Waters

To 5–6 l of the water add a little hydrochloric acid and evaporate to dryness; moisten the residue with concentrated hydrochloric acid, take up with water, and filter off the silicic acid. To the filtrate add a slight excess of ammonia; the phosphoric acid is usually completely thrown down in the form of phosphate of iron, aluminum, or alkaline earth. Dissolve the filtered and washed precipitate in nitric acid and determine the phosphoric acid according to one of the molybdate methods (pp. 390–394).

Remark. — If the mineral water does not contain much iron, aluminum, or alkaline-earth metal, but is rich in phosphoric acid and the alkalies, the precipitate produced by ammonia will not contain all the phosphoric acid. In such a case evaporate the hydrochloric acid solution from the silica several times to dryness with nitric acid, dissolve the residue in as little nitric acid as possible, and determine the phosphoric acid by one of the molybdate methods.

Recovery of Molybdenum Residue (H. Bornträger)*

To 250 ml of strong ammonia, in a large, wide-mouthed flask add the acid molybdenum filtrates. Either immediately or after standing some time, a crystalline deposit of nearly pure molybdic acid is formed.

* *Z. anal. Chem.*, **33**, 341 (1894).

When the flask is nearly full, make the solution nearly neutral, allow the precipitate to settle, and decant off the upper liquid containing only a small amount of molybdenum. Pour the residue upon a suction plate, wash once with water (not more, or the molybdic acid will dissolve) and suck as dry as possible. Dissolve the precipitate by warming with as little ammonia as possible, leaving behind a residue of iron and aluminum hydroxides, magnesia, and silicic acid. Filter these off and dilute the solution with distilled water until at 17° C it has a density of 1.11 = 14° Bé. It then contains 150 g of ammonium molybdate in a liter. If this solution is diluted with 4 times as much water a $3\frac{1}{2}$ per cent solution will be obtained.

Determination of Phosphorus in Organic Substances

The substance is decomposed by the method of Carius. By the action of the nitric acid in the closed tube the phosphorus is oxidized to phosphoric acid and this is determined as usual.

Separation of Phosphoric Acid from the Metals

1. Separation from the Metals of Groups I and II

Hydrogen sulfide is conducted into the hydrochloric acid solution,* by which means all the members of these groups are precipitated as sulfides while the phosphoric acid remains in solution.

2. Separation from the Metals of Group III

(*a*) The phosphoric acid is first precipitated as ammonium phosphomolybdate according to p. 392. In order to determine the metals, evaporate the solution containing molybdenum, but free from phosphoric acid, with sulfuric acid to a sirupy consistency, and carefully heat over a free flame until the nitric acid is expelled. After cooling, moisten the residue with hydrochloric acid and take up in water. Place the solution in a pressure flask, saturate with hydrogen sulfide, stopper the flask, and heat for some time on the water-bath; the molybdenum is precipitated as flocculent MoS_3. After cooling, slowly open the pressure flask and filter off the molybdenum sulfide. Analyze the filtrate, now free from phosphoric acid and molybdenum, for the metals as described on pp. 95–175.

(*b*) Separate the phosphoric acid as before, make the filtrate slightly ammoniacal, and saturate with hydrogen sulfide. After standing for some time the solution becomes reddish yellow in color, and the pre-

* When silver is present it is precipitated as silver chloride, filtered off, and the filtrate treated with hydrogen sulfide.

cipitate can then be filtered off. The metals of this group will be found in the precipitate while the molybdenum is in the filtrate in the form of its sulfo-salt.

Remark. — If nickel is present, some of it will remain in the filtrate with the molybdenum on account of the solubility of nickel sulfide in ammonium sulfide, so that method (*a*) will then give more accurate results. Vanadium (and tungsten) will also go with the molybdenum.

3. Separation of Phosphoric Acid from Iron, Cobalt, Manganese, and Zinc

If the solution contains iron in the ferric form, acidify with hydrochloric acid, saturate with hydrogen sulfide, and for each gram of the mixed oxides add 3 g of tartaric acid; make the solution slightly ammoniacal and allow to stand over night in a stoppered flask. The precipitate contains the metals as sulfides free from phosphoric acid. Filter, wash with water containing ammonium sulfide, dissolve in acid, and analyze according to pp. 95–175.

4. Separation from Chromic Acid

If the solution contains free alkali or alkali carbonate, make acid with nitric acid, then slightly alkaline with ammonia, and precipitate the phosphoric acid with "magnesia mixture" as described on p. 390.

5. Separation from Calcium, Strontium, Barium, Magnesium, and the Alkalies

Add the ammonium carbonate to the hydrochloric acid solution until a slight permanent turbidity* is produced, and dissolve this with a few drops of hydrochloric acid. Then add ferric chloride drop by drop until the liquid above the yellowish white precipitate of ferric phosphate becomes distinctly brown in color. Dilute the solution with water to a volume of 300–400 ml, boil for 1 minute, filter, and wash with water containing ammonium acetate. In the filtrate are the alkaline earths and alkalies, which, after expelling the ammonium salts by igniting the residue obtained after evaporating to dryness, are determined in the usual way (see pp. 55–95).

Determination of Phosphoric Anhydride in Apatite

Weigh out duplicate portions of the finely powdered mineral of 0.2–0.25 g, taking care to get the nearest tenth of a milligram as accu-

* If only alkalies are present there will be no turbidity; add the ammonium carbonate until the solution is neutral.

rately as possible. Heat in a covered 200-ml casserole with 15 ml of 6 N nitric acid. Evaporate to dryness on the steam-bath or hot plate, taking care to avoid spattering. Heat the residue for at least 15 minutes at 110–120° to dehydrate silica. Digest the residue with 25 ml of 6 N nitric acid, and heat a few minutes to dissolve the soluble material. Filter and wash with small portions of hot water, receiving the filtrate and washings in a 300-ml Erlenmeyer flask. Continue to wash until 5 ml of the filtrate will give no precipitate of calcium phosphate when neutralized with ammonia. If a precipitate is obtained, pour the test back into the filtrate. The volume of the solution should not exceed 100 ml at this point.

Neutralize the solution with ammonia and continue as described on p. 392.

THIOSULFURIC ACID, $H_2S_2O_3$. Mol. Wt. 114.14

Form: Barium Sulfate, $BaSO_4$

Treat the aqueous solution of the alkali thiosulfate with an ammoniacal solution of hydrogen peroxide, or with ammoniacal percarbonate solution, heat for some time on the water-bath, and then boil to destroy the excess of the reagent. Make the solution acid with hydrochloric acid and precipitate the sulfuric acid formed by the above treatment as barium sulfate. Two moles of $BaSO_4$ correspond to 1 mole of $H_2S_2O_3$.

A much better procedure for the estimation of thiosulfuric acid will be discussed under Iodometry, Part II.

The remaining acids of this group, arsenious, arsenic, vanadic, and chromic, have been discussed under the respective metals; periodic acid is analyzed in precisely the same way as iodic acid.

GROUP V

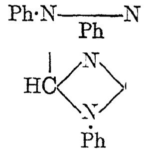
NITRIC, CHLORIC, AND PERCHLORIC ACIDS

NITRIC ACID, HNO_3. Mol. Wt. 63.02

Forms: Nitron Nitrate, $C_{20}H_{16}N_4 \cdot HNO_3$, Nitrogen Pentoxide, N_2O_5; Ammonia, NH_3; Nitric Oxide, NO, and Volumetrically

1. Determination of Nitric Acid as Nitron Nitrate*

The base diphenyl-endo-anilo-hydrotriazole, $C_{20}H_{16}N_4$



called *nitron* for short, forms a fairly insoluble, crystalline nitrate, $C_{20}H_{16}N_4 \cdot HNO_3$, which can be used for the separation and quantitative estimation of this acid. To prepare the reagent, nitron acetate, dissolve 10 g of nitron in 100 ml of 5 per cent acetic acid. It keeps fairly well in a dark bottle.

Procedure. — Take a sample equivalent to not more than 0.1 g of nitric acid, and dissolve in 80–100 ml of water containing 1 ml of glacial acetic acid. Heat the solution nearly to boiling and add at one time 10–12 ml of nitron acetate solution. Allow the precipitate to stand 24 hours in a dark place, then filter into a Gooch or Munroe crucible and drain as completely as possible from the pale yellow mother-liquor. Wash with 50 ml of ice-water saturated with nitron nitrate, added in small portions, and drain the precipitate well after each washing. Dry at 110° for 2 hours. The precipitate contains 16.79 per cent of HNO_3.

Remarks. — The method gives good results in the presence of sulfate and iodate ions. If large quantities of chloride are present a correction should be applied, as determined by an analysis with pure nitric acid and the same weight of chloride.

In 100 ml of very dilute acid, approximately the following weights of nitron salts dissolve: 0.0099 g of nitrate, 0.008 g of perchlorate, 0.017 g of iodide, 0.04 g of thiocyanate, 0.06 g of chromate, 0.12 g of chlorate, 0.19 g of nitrite, 0.61 g of bromide.

The results of the nitric acid determination are a little high rather than low, owing to occlusion of a little precipitant.

Besides the acids represented by the above difficultly soluble salts, ferro- and ferricyanic, picric, and oxalic acids interfere with the determination. Hydrobromic acid can be decomposed by adding chlorine water, drop by drop, to the boiling solution until the yellow color of bromine disappears, hydriodic acid by adding an excess of potassium iodate to the neutral solution and boiling off the iodine. Nitrous acid can be removed by dropping powdered hydrazine sulfate into the concentrated solution and chromic acid by reduction with hydrazine sulfate.

* M. Busch, *Ber.*, **38**, 861 (1905); A. Gutbier, *Z. angew. Chem.*, **1905**, 494.

2. Determination of Nitric Acid as Nitrogen Pentoxide*

This method is based upon the fact that, when an intimate mixture of a dry nitrate is heated with an excess of silica, nitrogen pentoxide is evolved and the amount is determined by the loss in weight:

$$2\,NaNO_3 + SiO_2 = Na_2SiO_3 + N_2O_5$$

This method cannot be used when any other volatile substance is present which is usually the case.

3. Determination of Nitric Acid as Ammonia†

The usual method for the determination of nitric acid is to reduce it in alkaline solution to ammonia by means of aluminum, zinc, or, best, Devarda's alloy (cf. Vol. I):

$$NO_3^- + 4\,Zn + 7\,OH^- \rightarrow 4\,ZnO_2^= + NH_3\uparrow + 2\,H_2O$$

After the reduction, the solution is distilled into a known quantity of acid and the excess of the acid found by titration, or the ammonia can be determined as ammonium chloroplatinate or as platinum (cf. p. 74, *b* and *c*).

Procedure. — Place about 0.5 g of the nitrate in a 500-ml Erlenmeyer flask (Fig. 92) and dissolve in 110 ml of water. To this solution add 5 ml of alcohol, 50 ml of caustic potash (*d.* 1.3), and 2–2.5 g of powdered Devarda's alloy. Or, instead of Devarda's alloy, use 5 g of well-washed zinc and 2 g of ferrous sulfate. Instead of the caustic potash solution, 80 ml of saturated sodium hydroxide solution can be substituted. At once connect the flask with the distillation apparatus shown in the figure. The left arm of the 250-ml Péligot tube, *A*, is connected by a curved tube with the middle bulb, so that a spurting back of the liquid is avoided. The delivery tube (of potash glass) connecting the flask *K* with the tube *A* is about 1 cm in diameter and is provided with a small opening at *o*, inside the flask, to prevent spurting of condensed liquid over into *A*. Place 20 ml of 0.5 *N* sulfuric acid in *A* and dilute so that the solution just reaches to each of the bulbs on the side. Place 5 ml of the acid in *B*, with a few drops of methyl orange indicator solution, and dilute in the same way. Connect the tubes *A* and *B* by means of a T-tube, of which the upper end is closed by a pinchcock upon a piece of rubber tubing, so that a piece of red litmus paper may be introduced here if it is desired to see whether NH_3 is escaping.

* Reich, *Z. Chem.*, **1**, 86 (1862).

† Devarda, *Z. anal. Chem.*, **33**, 113 (1894), Pannertz, *Z. anal. Chem.*, **39**, 318 (1900).

When all is ready, gently heat the contents of the flask K to start the reaction, then remove the flame and allow the reaction to proceed by itself. After an hour this will be shown to be complete by the cessation of the hydrogen evolution. Then slowly heat the liquid in K to boiling, and keep at this temperature until about half of the liquid has distilled over into A; this requires about half an hour. During the last 10 minutes pass a slow current of air through the tube r.

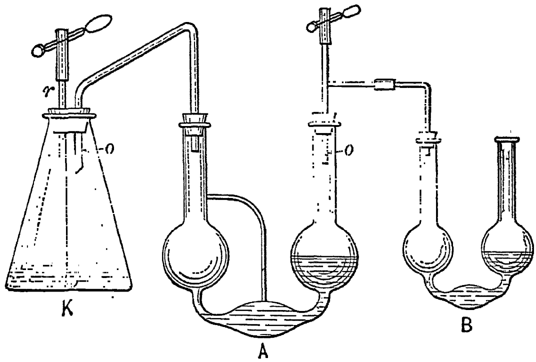


FIG. 92.

If the distillation has been correctly performed, all the ammonia will now be found in A; no trace should reach B, and the red litmus paper in the T-tube should show no tinge of blue.

When the distillation is finished, open the pinchcock at r and remove the flame. Add a little methyl orange to A whereby the liquid is colored red, pour the contents of B into A and rinse out B with water that is added to A. Finally titrate the excess of the sulfuric acid with $0.5\,N$ caustic alkali solution until a yellow end point is obtained. The amount of nitric acid is computed as follows:

If t milliliters of $0.5\,N$ base are used in the titration of a grams of substance, then $\frac{(25 - t) \times 3.151}{a}$ = per cent HNO_3 or $\frac{(25 - t) \times 2.700}{a}$ = per cent N_2O_5.

Determination of Nitric Acid as Nitric Oxide

*Method of Schlösing and Grandeau, modified by Tiemann and Schulze**

Principle. — If a nitrate is heated with ferrous chloride and hydrochloric acid, the nitric acid is reduced to nitric oxide:

$$NaNO_3 + 3\ FeCl_2 + 4\ HCl = NaCl + 3\ FeCl_3 + 2\ H_2O + NO$$

From the volume of the nitric oxide its weight can be calculated.

* *Z. anal. Chem.*, **9**, 401 (1870), and *Ber.*, **6**, 1041 (1873).

The method of Schlösing in its original form* was not much used on account of the apparatus required; but after being modified by Grandeau† it has become one of the best methods for the determination of nitric acid.

The apparatus necessary is shown in Fig. 93 and of a flask K fitted with a double-bored rubber stopper. Through one b, which reaches into the flask just to the lower surface of the other hole pass the tube a,‡ ending in a restriction about

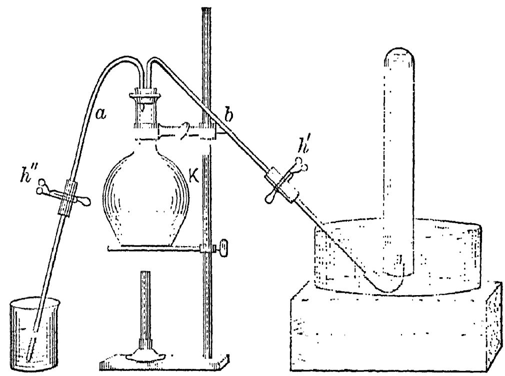


FIG. 93.

$1\frac{1}{2}$ cm below the stopper. Connect the tube b by means of a piece of rubber tubing 5 cm long, and provided with a pinchcock, with a second tube whose lower end reaches up into the measuring-tube and is covered with rubber tubing as is shown in the figure. In the same way connect the tube a with a straight tube.

Solutions required. 1. A nitrate solution of known strength; dissolve 2.022 g of recrystallized potassium nitrate, dried at 160°, in 1 l of water. At 0° and 760 mm pressure, 50 ml of this solution evolve 22.39 ml of NO.

2. Ferrous chloride solution. Dissolve 20 g of iron (nails) in 100 ml of concentrated hydrochloric acid.

3. Six normal hydrochloric acid, *d.* 1.1.

Procedure. — Pour 10 ml of water into K and mark its upper level on the outside of the flask with a colored pencil, then add 40 ml more and mark its position.

Now pour out the water and add from a pipet exactly 50 ml of the standard nitrate solution to K, insert the stopper with the delivery tubing in place, and open the pinchcocks h' and h''. Heat the contents of the flask to boiling with a free flame until no more bubbles of air escape from the lower end of b into the bath containing boiled water.

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* *Annal. chim. et phys.*, [3], **40**, 479 (1853).

† Grandeau, *Analyse chimique appliquée à l'agriculture.*

‡ Grandeau used a separatory funnel instead of the tube a; the latter was proposed by Tiemann and Schulze.

To make sure that all the air is expelled from the apparatus, pinch the rubber tubing at h' with the thumb and finger; if no air is present, the liquid will quickly rise in b, exerting a noticeable pressure. Then close the pinchcock h' and continue the boiling until the 50 ml has been reduced to a volume of 10 ml; then remove the flame and close the pinchcock h''. The lower end of a, which dips into distilled water, is immediately filled up to the pinchcock. The vapors in the flask condense, forming a vacuum, as shown by the closing together of the rubber tubing at h' and h''.

Pour 30 ml of the ferrous chloride solution into a beaker and mark the upper level on the outside with a colored pencil, add 20 ml more and note the position in the beaker again. Place the lower end of the tube a in the ferrous chloride solution so that it reaches below the lower mark on the beaker, and, by opening h'', allow 20 ml of the solution to pass into the flask K. Then replace the beaker containing the ferrous chloride with one containing boiled water. The tube a should not extend vertically into the water, but should be inclined as much as possible. The specifically heavier ferrous chloride solution in the tube passes into the water, and the water takes its place. When the lower end of a has become filled with pure water in this way, dip it into a beaker containing $6\,N$ hydrochloric acid and allow about 20 ml of the acid to flow into K, and finally add 3–4 ml of water to replace the acid in a. Now fill a 50-ml measuring-cylinder with boiled water, place over the lower end of b as shown in the figure, and heat the contents of the flask K 15 minutes on the water-bath,* then boil with a free flame. As soon as the compressed rubber tubing begins to expand open h', but at the same time pinch the rubber tubing between the thumb and finger. When the liquid no longer rises in b, remove the hand from the rubber tubing and allow the nitric oxide to collect slowly in the measuring-tube. After half of the liquid has evaporated, no further evolution of nitric oxide is to be noticed, although the brown color of the solution shows that the gas has not been completely expelled. To accomplish this, remove the flame, close h', and allow the liquid in K to cool. By means of the vacuum thus produced the remainder of the nitric oxide is expelled from the solution. Repeat the boiling once more, with the same precautions, until the lower mark is reached. Remove the flame, close h', and place the measuring-tube containing the nitric oxide in a cylinder containing pure water at the temperature of the room. To prevent the tube containing the gas from sinking, encase its upper end in a large cork so that it floats on the

* The heating on the water-bath is necessary, as otherwise a little nitric acid will distil over and not be reduced. A. Wegelin, *Inaug. Dissert.* Zürich, 1907.

water. After standing 15–20 minutes raise the tube, by cork, until the level of the liquid within stands at the sa that in the cylinder without, and read the volume of the same time take the temperature of tl eac

If the temperature was $t°$, the barometer reading B milli the tension of aqueous vapor at $t°$; 0° and 760 mm pressure is

$$V_0 = \frac{V(B - w)}{760\ (273 + t)}$$

Now 50 ml of the standard potassium nitrate solution contain 0.1011 g of KNO_3 corresponding to 0.05401 g of N_2O_5, so that the volume V_0 of the nitric oxide corresponds to 0.05401 g of N_2O_5. Repeat the experiment several times and use the mean value. It is not permi to assume that 0.1011 g of KNO_3 will furnish exactly 22.39 ml of : oxide as a little always remains in the flask.

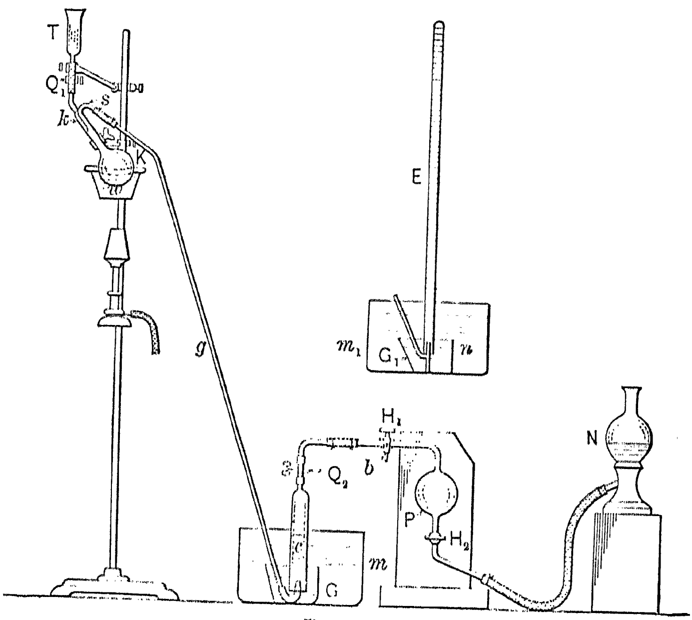

FIG. 94.

Now carry out the same procedure with 50 ml of the solution of the unknown nitrate, which should be prepared so that the amount of nitric oxide evolved will be about the same as that from 50 ml of the standard solution.

Good results are obtained by this method but the rubber stoppers are attacked quite badly and analyses are sometimes spoiled by not opening the pinchcock h' at just the right time. These difficulties have been overcome by Wegelin* in the apparatus shown in Fig. 94. The decomposition flask K has a capacity of about 120 ml. Its neck is about 9 cm long, and into it are fused glass tubes k and s connecting the flask with the funnel T and the delivery tubing G. The results are a little too high by this method so that it is advisable to carry out the standardization with about the same quantity of nitrate as taken for actual analysis.

Modified Procedure. — Through the funnel T pour the concentrated solution of the weighed nitrate and rinse out the funnel with 50 ml of water. Close the stopcock a, and boil the liquid in K. Have the 75 cm long tube g in place, dipping under mercury in the small dish G, but do not have the tube C over the end of the tubing. After half the liquid in K has boiled away, remove the flame and allow mercury to suck up into the tube g. Mark the height of the mercury; if it does not fall during 15 minutes, the apparatus is tight. Again heat the liquid in K to boiling, and when steam escapes, at the bottom of g, open the stopcock Q_1 and drive out all air from the tubing k. Boil, with Q_1 open, until the liquid in K is reduced to 10 ml as shown by the mark etched on the flask. Then close Q_1 and allow the liquid in K to cool a little. Pour 20 ml of standard ferrous chloride solution into T and cause it to flow into K by carefully opening the stopcock but taking care not to let any air in. Rinse out T with 80 ml of $6N$ hydrochloric acid and place the cylinder C, filled with mercury, over the end of the tubing g. Heat the contents of K 20 minutes, with the water-bath W in place, and then boil with a free flame until the volume of liquid is reduced to 10 ml. Remove the flame and transfer the gas in C into the Drehschmidt pipet, P, by lowering the leveling-bulb N, and opening H_1 and Q_2. Also introduce 0.5 ml of 33 per cent caustic potash solution through the tip of the stopcock H_1. This serves to absorb hydrochloric acid gas. After a little while, transfer the gas to a gas buret and measure it over mercury or over water.

It is also permissible to collect the gas over water. In that case have the 75-cm tube g end in a 6–7 cm T-tube G_1 open at both ends. Fill the dish n with mercury till level with the upper end of the T-tube and place n in the dish m_1 containing water.

* *Doctorate Thesis*, Zürich, 1907.

Determination of Nitric Acid in a Drinking-water

Evaporate 100–300 ml of the water to 40–50 ml in a porcelain dish, add a few drops of methyl orange indicator solution, and dilute hydrochloric acid, free from nitrate, until the solution is pink. Now add sodium carbonate solution until the liquid is barely alkaline and wash the contents of the flask into the decomposition flask *K*, Fig. 93, and analyze as described on p. 404, but collect the gas over 10 per cent sodium hydroxide solution, to make sure that the carbonic acid is completely absorbed.

After the experiment with the water to be analyzed, repeat with an amount of the standard solution sufficient to evolve about the same quantity of nitric oxide.

Remark. — In drinking-water the neutralization of the evaporated sample is not absolutely necessary, except with alkaline mineral waters; in that case the introduction of the hydrochloric acid would otherwise cause such a violent evolution of carbon dioxide that the flask might crack.

CHLORIC ACID, $HClO_3$. Mol. Wt. 84.47

Form: Silver Chloride, AgCl, besides volumetric and gasometric methods

To determine chloric acid as silver chloride it must previously be reduced to chloride by means of ferrous sulfate or zinc.

Reduction by Means of Ferrous Sulfate

Dissolve 0.3 g of the salt in 100 ml of water, add 50 ml of a 10 per cent solution of crystallized ferrous sulfate, heat with constant stirring till the solution begins to boil, and keep at this temperature for 15 minutes. After cooling, add nitric acid until the deposited basic ferric salt is dissolved, precipitate the chloride by means of silver nitrate, and weigh after the usual treatment.

One gram of silver chloride corresponds to 0.8550 g. $KClO_3$.

Reduction by Zinc

Although chlorates are reduced in neutral solution by means of zinc or Devarda's alloy, it is not advisable to effect the reduction in this way for quantitative purposes. The same end is reached more expeditiously by adding zinc-dust to an acetic acid solution. Treat the dilute chlorate solution with acetic acid until it reacts distinctly acid, add an excess of powdered zinc, and boil the solution for 1 hour. After cooling, add nitric acid in sufficient quantity to dissolve all the

excess of zinc, filter if necessary, and determine the chloride as silver salt (p. 300).

Remark. — Both of the above methods afford exact results, but the former is to be preferred, for it requires less time.

Chlorates are not decomposed quantitatively into chlorides by ignition in open vessels or in a current of carbon dioxide. Some chlorine and a little alkali is always lost, so that even when the residue is evaporated with hydrochloric acid, too low results are obtained.

According to the two following methods, the decomposition of alkali chlorate into chloride is quantitative.

(a) By Evaporation with Hydrochloric Acid

Cover 0.3 g of chlorate in a weighed porcelain crucible with 1.5 N hydrochloric acid. Place a watch glass upon the crucible, and heat the contents on the water-bath until the evolution of chlorine ceases. Rinse off the lower surface of the watch glass, and evaporate the contents of the crucible to dryness on the water-bath. Replace the cover and gently ignite over a free flame until the decrepitation ceases. After cooling in a desiccator, again weigh the crucible.

(b) By Ignition with Ammonium Chloride

Mix the alkali chlorate in a porcelain crucible with 3 times as much pure ammonium chloride, cover with a watch glass, heat over a free flame, keep in constant motion until the ammonium chloride is completely removed, and weigh the residual alkali chloride.

PERCHLORIC ACID, $HClO_4$. Mol. Wt. 100.47

Form: Silver Chloride, AgCl

Perchlorates cannot be reduced to chloride by means of ferrous sulfate, zinc, or by repeated evaporation with concentrated hydrochloric acid.* On ignition, some chlorine and alkali chloride and probably a little perchloric acid are lost, so that an error amounting to as much as 1 per cent may be expected. On the other hand, Winteler has shown that perchlorates may be changed to chlorides by heating with concentrated nitric acid and silver nitrate in a closed tube (see Carius' method for determining chlorine in organic substances, p. 303), and L. Blangey found that ignition with ammonium chloride would accomplish the same result. With 0.3 g of perchlorate and 2 g of am-

* On evaporating with hydrochloric acid there is a loss without any evolution of chlorine; it is due to the volatilization of small amounts of perchloric acid.

monium chloride, 90 minutes should be sufficient for complete reduction.

Decomposition of Perchlorates by Ignition with Ammonium Chloride

By twice igniting an intimate mixture of 0.5 g potassium perchlorate with 1.5–2 g of ammonium chloride in a *platinum* crucible covered with a watch glass, the perchlorate is completely changed to chloride. Care should be taken not to melt the residual chloride, for then the platinum is attacked, although the accuracy of the results is not affected. The reduction cannot be accomplished completely in a porcelain crucible unless platinum is present as catalyzer. If 0.5 g of alkali perchlorate is mixed with 1 g of ammonium chloride, and 1 ml of chloroplatinic acid solution (0.0918 g Pt) is added, a complete reduction can be accomplished by igniting and repeating with 2 more additions of ammonium chloride.

Determination of Perchloric Acid in the Presence of Chloric Acid

In one portion reduce the chlorate, as described on p. 408, with ferrous sulfate, and determine the chloride formed as silver chloride. Ignite a second portion in an old platinum crucible (or in one of porcelain with the addition of 1 ml of chloroplatinic acid) and 3 times as much ammonium chloride (as described above). In this way the total amount of chlorine is obtained, and from these data the amount of each acid can be calculated.

Determination of Perchloric, Chloric, and Hydrochloric Acids in the Presence of One Another

The three acids are assumed to be present in the form of their alkali salts.

In one portion determine the chloride-chlorine by precipitation with silver nitrate. In a second sample determine the chlorate and chloride-chlorine after the chlorate has been reduced to chloride by means of ferrous sulfate. Determine the total amount of chlorine present in a third portion after ignition with ammonium chloride.

GROUP VI

SULFURIC, HYDROFLUORIC, AND FLUOSILICIC ACIDS

SULFURIC ACID, H_2SO_4. Mol. Wt. 98.08

Form: Barium Sulfate, $BaSO_4$

Theoretically the gravimetric determination of sulfuric acid is extremely simple, it being only necessary to precipitate with barium chloride, filter, and weigh the barium sulfate. Practically, however, it is a process connected with many difficulties.

According to the manner of precipitating barium sulfate, the composition of the precipitate varies in such a way that sometimes the results are too high and sometimes too low.

Errors Which May Occur in the Precipitation of Barium Sulfate

I. In the Precipitation of Barium Chloride with Pure Sulfuric Acid

If a dilute, slightly acid solution of barium chloride is treated at the boiling temperature with an excess of dilute sulfuric acid, the precipitate contains all the barium except a very small, negligible amount. If, however, the precipitate is weighed, the result is invariably too low; and this is true even when the solution is evaporated to dryness in order to recover the last traces of barium. The precipitate always contains barium chloride in a form which cannot be removed by washing. A mixture, therefore, of barium sulfate and barium chloride is weighed, and as the molecular weight of the chloride is less than that of the sulfate, the result must be too low. To obtain accurate results, the chlorine combined with barium in the precipitate must be replaced by SO_4; and this can be accomplished by moistening the precipitate with concentrated sulfuric acid, and heating until the excess of the acid is removed by volatilization.

Not only is barium *chloride* carried down with barium sulfate, but all barium salts as well, especially the chlorate and nitrate. These are, however, readily changed to sulfate by the above treatment with concentrated sulfuric acid. It is immaterial in the estimation of barium how the precipitation is effected; whether the sulfuric acid is added quickly, or drop by drop, the results are always the same.

II. In the Precipitation of Pure Sulfuric Acid with Barium Chloride

This is the reverse process, but here it is not a matter of indifference whether the barium chloride is added slowly, drop by drop, or rapidly all at one time. In the first instance, the results are very near the truth

without applying any correction; in the second, too high results are obtained, because by the rapid addition of the reagent more barium chloride is carried down with the precipitate than when the reagent is added very slowly.

To obtain the true weight of barium sulfate, it is often necessary to make a deduction for the amount of barium chloride contained in the precipitate and to add the weight of barium sulfate remaining in solution.

The chlorine contained in the precipitate can be determined in several different ways.

1. Fuse the precipitate with 4 times as much pure sodium carbonate, extract the melt with hot water, filter, make the filtrate acid with nitric acid, and precipitate the chlorine with silver nitrate. Filter and weigh.

2. Still more accurate is the process of Hulett and Duschak.* Place the ignited precipitate of barium sulfate in a U-tube of which one arm is drawn out into a thin, right-angled, gas delivery tube. Add concentrated sulfuric acid to the precipitate and heat the mixture by placing the U-tube in hot water. The barium sulfate dissolves readily in the hot, concentrated sulfuric acid, and the barium chloride present is decomposed. To determine the amount of hydrochloric acid set free, pass a slow stream of air, which has been washed with caustic potash solution, through the tube, with the drawn-out end of the latter dipping into a stout test-tube containing $0.01\,N$ silver nitrate solution. After 2–2.5 hours all the hydrochloric acid will have been expelled from the sulfuric acid.

Remove the decomposition apparatus, rinse out the gas delivery tube with a little water, and determine the silver remaining in solution volumetrically (cf. Volhard Method).

For the determination of the dissolved barium sulfate, evaporate the filtrate from the first precipitation to dryness, moisten the residue with a few drops of concentrated hydrochloric acid, take up with water, filter off the slight precipitate of barium sulfate, and weigh. During all such work take care to prevent sulfuric acid contamination from the air in the laboratory. The evaporation should, therefore, take place on the steam-bath or steam-table.

Calculation of the True Weight of Barium Sulfate. — If the weight of the first precipitate of crude barium sulfate is a, the weight of the barium chloride contained in this precipitate, as determined by titration of the amount of chlorine, is b, and the amount of barium sulfate in solution is c, then $a - b + c$ represents the weight of pure barium sulfate.

* *Z. anorg. Chem.*, **40**, 196 (1904).

Experience has shown, however, that when pure sulfuric acid is precipitated by means of dilute barium chloride solution added drop by drop, the errors *b* and *c* are approximately equal and counterbalance each other so that the weight *a* is very close to that of the pure barium sulfate.

III. In the Precipitation of Sulfates with Barium Chloride

Here the relations are far more complicated than in the precipitation of pure sulfuric acid, partly because the barium sulfate is more soluble in salt solutions than in water containing a little acid, and partly because of the tendency of barium sulfate to occlude not only barium chloride but many other salts as well. Solutions of chromium sulfate are either violet or green. From the boiling-hot green solution only one-third of the sulfuric acid is precipitated, the remainder probably being present in the form of a complex chromium sulfate cation;* on cooling, the green solution gradually becomes violet, and after some time all the sulfuric acid is precipitated. The precipitation of barium sulfate in the presence of ferric iron has been much studied. In the boiling-hot solution, not all the sulfuric acid is precipitated and considerable iron is thrown down with the barium sulfate, and furthermore, the precipitate then loses SO_3 on ignition. Since ferric oxide weighs less than an equivalent weight of barium sulfate sometimes the results are as much as 10 per cent too low. On the other hand, Küster, and Thiel† were able to get satisfactory results (1) by precipitating the sulfuric acid from such a solution in the cold, (2) by slowly adding the ferric chloride and sulfuric acid solution to the hot solution of barium chloride, or (3) by precipitating the iron by an excess of ammonia, heating, and adding barium chloride to the solution without filtering off the ferric hydroxide, and finally dissolving the latter in dilute hydrochloric acid.

Most chemists, however, deem it advisable to remove trivalent metals before attempting to determine the sulfuric acid. This is accomplished in the case of ferric iron by adding a liberal excess of ammonia to the dilute, slightly acid solution which is at a temperature of about 70°. If 5–7 ml of concentrated ammonia (*d.* 0.90) is added in excess of the amount required for neutralization,‡ the precipitate is not likely to contain any basic ferric sulfate. If, on the other hand, the solution is barely neutralized with ammonia, the precipitate will invariably contain some sulfate.

The bivalent metals are occluded to a much less extent, so that it is

* Recoura, *Compt. rend.*, **113**, 857; **114**, 477.

† *Z. anorg. Chem.*, **22**, 424.

‡ Pattinson, *J. Soc. Chem. Ind.*, **24**, 7.

not, as a rule, necessary to remove them. On the other hand, in the presence of considerable amounts of bivalent metal with relatively small amounts of sulfuric acid, the error arising from occlusion is likely to be large, so that it is better to remove the bivalent metals in such cases. The error caused by ferric salts can be largely overcome by reducing the iron with zinc.

In the presence of alkali nitrate or chlorate the barium sulfate precipitate will contain considerable quantities of barium chlorate and nitrate which it is impossible to remove by washing with hot water. These acids, therefore, must be decomposed by evaporation with hydrochloric acid before attempting to precipitate the sulfuric acid.

In ordinary chemical practice it is usually a question of determining sulfuric acid in a solution containing considerable amounts of ammonium or alkali chloride, ammonium or alkali sulfate, and some free hydrochloric acid. Now ammonium and alkali sulfates are also occluded by barium sulfate, and the amount of occlusion increases as the solution is more concentrated with respect to these substances. For this reason it is evident that barium sulfate should always be precipitated in a dilute solution. On the other hand, if the solution is too dilute or very concentrated the crystals are so small that they will run through a filter. A small amount of free hydrochloric acid is indispensable, but larger amounts have a solvent effect upon the precipitate. One might think that adsorbed ammonium chloride would do no harm, but it has been found to cause some volatilization of SO_3 during ignition.

For an amount of sulfuric acid corresponding to 1–2 g of barium sulfate, the precipitation should take place in a volume of 350–400 ml and in the presence of 1 ml of $12\,N$ hydrochloric acid.

If a *neutral* solution is at hand, dilute to a volume of 350 ml and add 1 ml of concentrated hydrochloric acid. Carefully neutralize an *alkaline* solution with hydrochloric acid, using methyl orange as indicator, add 1 ml of concentrated hydrochloric acid in excess, and dilute the solution to 350 ml.

Finally, in the case of an *acid* solution, either evaporate to dryness, moisten the residue with 1 ml of concentrated hydrochloric acid, and add 350 ml of water, or, with methyl orange as indicator, neutralize the solution with ammonia, add 1 ml of concentrated hydrochloric acid, and dilute to 350 ml.

After the solution has been prepared in accordance with the above directions it is ready for the

Precipitation of Sulfuric Acid in the Presence of Ammonium or Alkali Salts according to E. Hintz and H. Weber

Heat the solution to boiling, and for each 0.12 g of sulfur use 100 ml of 0.1 *N* barium chloride solution. Heat to boiling, and add the hot reagent all at once, stirring the hot solution of the sulfate. After the solution has stood for half an hour, best in a warm place, filter, wash with hot water, and ignite (cf. p. 88). The use of a Gooch or Munroe crucible is to be recommended.

Remarks. — In the presence of ammonium salts the precipitation of the barium sulfate should not be effected by the slow addition of the barium chloride, as is otherwise desirable, for, as Hintz and Weber have shown, this leads to low results, whereas the occlusion caused by the rapid addition of the barium chloride counterbalances this error.

Under no circumstances should a precipitate of barium sulfate be heated over a blast lamp, for then sulfuric anhydride is evolved from the barium sulfate.

To explain the occlusion of barium chloride by barium sulfate, Hulett and Duschak* have suggested that perhaps the precipitate may contain salts such as $BaCl \cdot HSO_4$, $(BaCl)_2SO_4$, and $Ba(HSO_4)_2$, and Folin† believes this is so because some of his precipitates have lost SO_3 on ignition whereas others have lost HCl. He also suggests the possibility of salts such as $Ba(KSO_4)_2$ being precipitated.

Determination of Sulfuric Acid in Insoluble Sulfates

Calcium and strontium sulfates can be decomposed by long digestion with ammonium carbonate solution. Barium sulfate is decomposed so slowly by boiling with a soluble carbonate that it is best to mix with 4 times as much sodium carbonate, fuse in a platinum crucible, extract the melt with water, and wash the barium carbonate residue with sodium carbonate solution. Make the filtrate acid with hydrochloric acid, boil off the carbon dioxide, and precipitate the sulfuric acid as usual.

Lead sulfate can be decomposed by boiling with sodium carbonate solution; after cooling, saturate the solution with carbon dioxide and filter. The lead remains behind as carbonate; the filtrate contains all the sulfuric acid.

For the determination of sulfuric acid in silicates, fuse the finely powdered substance with 6 times as much sodium carbonate, extract the melt with water, make the filtrate acid with hydrochloric acid, and evaporate to dryness to dehydrate the silica. Moisten the residue with a little concentrated hydrochloric acid, take up in hot water, and filter off the silicic acid. Determine the sulfuric acid in this filtrate.

* *Z. anorg. Chem.*, **40**, 196 (1904).

† *J. Biol. Chem.*, **1**, 131 (1905).

Determination of Sulfuric Acid in the Presence of Soluble Sulfides

Place the substance in a flask, replace the air by carbon dioxide, add dilute hydrochloric acid, and boil the solution while passing carbon dioxide through it until all the sulfide has been expelled. Then precipitate the sulfuric acid from the solution.

This determination is used in the analysis of cements but the hydrochloric acid solution of the cement will contain much calcium as well as iron and aluminum. It is best to precipitate these metals by the addition of ammonia and ammonium carbonate and determine the sulfuric acid in the filtrate.

If it is desired to determine the amount of sulfide-sulfur, cover the substance with concentrated hydrochloric acid that is saturated with liquid bromine, dilute, add hydrochloric acid and boil the solution to expel the excess of the bromine. Precipitate the iron, aluminum, and calcium by ammonia and ammonium carbonate, and determine the total sulfur in the filtrate. The difference between the two results represents the amount of sulfur present as sulfide. For the volumetric determination of sulfuric acid consult Part II.

HYDROFLUORIC ACID, HF. Mol. Wt. 20.01

Forms: Calcium Fluoride, CaF_2; Silicon Fluoride, SiF_4, besides volumetric and gasometric methods

1. Determination as Calcium Fluoride

If the solution contains free hydrofluoric acid or an acid fluoride, add sodium carbonate until the reaction is alkaline and from one-fourth to one-fifth as much more in excess. By the excess of sodium carbonate the subsequent precipitate of calcium fluoride will contain calcium carbonate, which renders the precipitate easy to filter. A pure precipitate of calcium fluoride is slimy and the pores of the filter become so clogged that it is almost impossible to complete the filtration. To solutions of neutral fluorides, add about 1 ml of $2N$ sodium carbonate solution. Heat the alkaline solution to boiling, add an excess of calcium chloride solution, filter, and thoroughly wash the precipitate of calcium fluoride and carbonate with hot water. Dry the precipitate, transfer as much of it as possible to a platinum crucible, add the ash of the filter, and ignite the contents of the crucible. The ignition makes the CaF_2 denser and hence easier to filter. After cooling, cover the mass with an excess of dilute acetic acid; this changes the lime to the soluble acetate, but does not affect the fluoride. Evaporate the mix-

ture to dryness on the water-bath; moisten the residue with water and a few drops of 6 N acetic acid. Filter off the insoluble calcium fluoride, wash, and dry. Transfer as much of the dried CaF_2 to the crucible as possible, burn the filter paper, add its ash, and after ignition weigh the crucible. To confirm the result treat the substance with a little concentrated sulfuric acid (added cautiously), evaporate off the excess of the acid, once more ignite, and weigh the contents of the crucible as calcium sulfate. Calcium fluoride is not volatilized in an open platinum crucible heated over a Bunsen burner. Heated over the blast lamp, there is appreciable volatilization.

One gram CaF_2 yields 1.7436 g $CaSO_4$.

Remark. — The results are usually a little low on account of the solubility of calcium fluoride; 100 ml of water dissolves 0.0016 g and 100 ml of 1.5 N acetic acid dissolves 0.011 g CaF_2 at the temperature of the water-bath.

Example: Determination of Fluorine in Calcium Fluoride. — Calcium fluoride alone is not decomposed completely by fusing with sodium carbonate; but if mixed with $2\frac{1}{2}$ times as much silica and then fused with 6 times as much sodium-potassium carbonate, the greater part of the silicic acid and all of the fluorine will be changed to soluble alkali salts, while the calcium will be left as insoluble calcium carbonate. The mixture must be heated gradually (best in a platinum dish), as otherwise the evolution of carbon dioxide may cause the melt to boil over. The thin liquid fusion soon changes to a thick paste or only sinters somewhat. On raising the temperature, it is almost impossible to further melt this mass, and it is not necessary. In fact, too high a temperature is to be avoided on account of the danger of losing some alkali fluoride by volatilization. The reaction is complete when there is no further evolution of carbon dioxide. After cooling, treat the melt with water, filter off the insoluble residue and thoroughly wash with hot water. Remove silicic acid by adding 4 g of ammonium carbonate,* heat for some time at about 40°, allow to stand over night, and in the morning filter off the voluminous prècipitate. Wash it with 2 per cent ammonium carbonate solution (pure water will give a turbid filtrate). The filtrate now contains only a small amount of silicic acid. Evaporate almost to dryness on the water-bath,† dilute with a little water, and add a few drops of phenolphthalein indicator solution. The liquid is colored pink by the indicator; add enough nitric acid to make it colorless. Heat the solution to boiling, which causes the reappearance of the pink color. After cooling again discharge the color with nitric acid, and repeat this operation until finally the addition of $1–1\frac{1}{2}$ ml of 2 N nitric acid is sufficient to effect the decolorization.

The solution still contains a little silicic acid which can be removed, as recommended by Berzelius, by precipitating with 2 ml of ammoniacal zinc oxide. To prepare this, add sodium carbonate to a neutral zinc solution, heat to boiling, filter and wash with hot water. Dissolve the precipitate in the Schaffgottsche ammonium

* Before adding the ammonium carbonate, the greater part of the alkali carbonate should be neutralized with dilute hydrochloric acid, but care should be taken not to make the solution acid.

† The liquid foams during the evaporation owing to the decomposition of the excess of ammonium carbonate; the evaporating-dish should be covered with a watch glass until the evolution of carbon dioxide ceases.

carbonate reagent (p. 84). After the addition of the ammoniacal zinc solution, heat to boiling till the ammonia is wholly expelled, filter, and wash the precipitate with hot water.

The above-prescribed use of nitric acid instead of hydrochloric acid is necessary because some phosphate is likely to be present which must be removed. To the still alkaline solution, add silver nitrate in slight excess. This serves to precipitate the phosphate (chromate), chloride, and carbonate of silver. Heat slightly, filter, and wash with hot water. Remove the excess silver by adding a little sodium chloride solution. Boil to coagulate, filter, and wash the precipitate with hot water. Add 1 ml of 2 *N* sodium carbonate solution and precipitate with calcium chloride as described on p. 416.

Determination of Silica and Fluorine in Glasses and Enamels

The method just described is tedious. Hoffman and Lundell* have modified the procedure, so that the determination of fluorine and silica can be made in silicates in much less time and with greater accuracy. Instead of precipitating the fluorine as calcium fluoride, it is obtained as lead chlorofluoride, PbClF, which can be dissolved in dilute nitric acid and the chloride content determined by titration with silver nitrate (see Volhard Method).

The precipitation of lead chlorofluoride should take place in a solution of p_H 3.5–5.6. The presence of as little as 0.5 mg of aluminum causes low results as does more than 50 mg of boron, 0.5 g of ammonium, or 10 g of sodium or potassium. In the volumetric procedure small quantities of silica, phosphates, or sulfates do no harm. Phosphate may cause the filtrate from the lead chlorofluoride precipitate to become turbid.

Lead chlorofluoride is appreciably soluble in water (0.325 g in 1 l of water at 25°) but is practically insoluble in a saturated solution of lead chloride in cold water. Moreover, in washing the precipitate with water, less of the precipitate dissolves than corresponds to the formation of a saturated solution.

Procedure. — Fuse 0.5 g of sample, in a platinum crucible with about 5 g of sodium carbonate. Leach the cooled melt with hot water and filter when its disintegration is complete. Wash back the insoluble residue into the beaker used for the leaching, add 50 ml of 2 per cent sodium carbonate solution, boil a few minutes, filter, and wash with hot water until a drop of the filtrate is neutral to red litmus paper. The residue will contain a part of the silica in the original sample and must be saved for its determination.

To the combined filtrates, at a volume of about 300 ml add zinc nitrate solution which has been prepared by dissolving 1 g of zinc oxide in 20 ml of 1.5 *N* nitric acid. Boil 1 minute and filter off the precipitate. Wash thoroughly with hot water and save this precipitate also for the silica determination.

Add a few drops of methyl red indicator solution to the filtrate and nearly neutralize with nitric acid. Evaporate to about 200 ml, but

* *Bur. Standards J. Research*, **3**, 58 (1929).

take care that the solution remains slightly alkaline. After this evaporation, however, add 1.5 N nitric acid until the color of the solution is a very faint pink. Now add an ammoniacal zincate solution prepared by treating 1.0 g of zinc oxide and 2.0 g of ammonium carbonate with 20 ml of water and 2 ml of concentrated NH_4OH and digesting on the water-bath until the solution is clear, and heat in a covered platinum dish until there is no more odor of ammonia, which usually requires evaporation to about 50 ml. Add 50 ml of warm water, stir, digest a few minutes, filter, and wash the precipitate with cold water. It contains the last traces of silica, and the filtrate contains all the fluorine.

Determination of Silica. — With the aid of a jet of 0.6 N hydrochloric acid, transfer the three precipitates obtained above to the dish in which the last precipitation was made. Ignite the filters and add any residue to the contents of the dish. Now add 25 ml of concentrated hydrochloric acid and evaporate to dryness on the steam-bath. Remove the dish from the steam-bath, moisten the residue with 10 ml of concentrated hydrochloric acid, warm slightly, and then add 100 to 150 ml of hot water. Digest on the steam-bath for 15 minutes, filter, and wash thoroughly with hot dilute 0.6 N hydrochloric acid and then with hot water. Return the filtrate and washings to the dish in which the evaporation was made, add 10 ml of concentrated sulfuric acid, and evaporate until fumes of sulfuric acid are evolved. Allow to cool, add 100 to 150 ml of water, heat carefully until salts are in solution, filter, and wash with hot water. Place the two papers containing the silica in a weighed platinum crucible, heat slowly until dry, next char the paper without inflaming, burn off the carbon at as low a temperature as possible, and finally ignite to about 1000° C. Cool in a desiccator, weigh, and repeat the heating until a constant weight is obtained. Determine the silica by treatment with hydrofluoric and sulfuric acids in the usual manner.

Determination of Fluorine. — Take the filtrate from which the three impure silica precipitates were removed and add a few drops of bromophenol blue indicator solution.* Adjust the volume of the solution to 250 ml, add dilute nitric acid until the color changes to yellow, and then add dilute sodium hydroxide until it changes just to blue. Now add 2 ml of 6 N hydrochloric acid and 5 g of solid lead nitrate, and heat on the steam-bath. As soon as the lead nitrate is in solution, add 5 g of solid sodium acetate, stir vigorously, and digest on the steam-bath for $\frac{1}{2}$ hour with occasional stirring. Allow to stand at least 4 hours at room temperature and then decant the solution through a paper of

* Prepared by triturating 0.4 g of the dry powder with 6 ml of 0.1 N NaOH and diluting to 100 ml.

close texture. Wash the precipitate, beaker, and paper once with cold water, then 4 to 5 times with a cool saturated solution of lead chlorofluoride and then once more with cold water.

Transfer the precipitate and paper to the beaker in which the precipitation was made, stir the paper to a pulp, add 100 ml of $0.75\,N$ nitric acid, and heat on the steam-bath until the precipitate is dissolved. Then add a slight excess of standard, approximately $0.2\,N$ solution of silver nitrate, carefully noting the volume. Digest on the steam-bath for $\frac{1}{2}$ hour, cool to room temperature while protected from the light, filter, wash with cold water, and determine the silver nitrate in the filtrate by titrating with of a standard solution of potassium thiocyanate (see Volumetric Determination of Silver).*

2. Determination as Silicon Fluoride

This method, proposed by Fresenius, depends upon the fact that many fluorides are decomposed by the action of concentrated sulfuric acid and silica; the fluorine escapes as silicon fluoride, which can be absorbed and weighed.

Procedure. — The same reagents and a very similar apparatus to that described on p. 421 are required for this determination, except that in place of the Péligot tubes (Fig. 95, p. 422) two weighed, glass-stoppered U-tubes are used, of which the first is filled with moistened pieces of pumice, and the second has one arm filled with soda-lime and the other with calcium chloride. The analysis is carried out in exactly the same way as is described for the Penfield method (see below) but at the end of the experiment the two U-tubes are weighed. The increase in weight represents the amount of SiF_4, and from this the amount of fluorine present is calculated as follows: Assume that a grams of calcium fluoride yielded p grams of SiF_4. The treatment with the concentrated sulfuric acid caused the following reaction to take place:

$$2\,CaF_2 + 2\,H_2SO_4 + SiO_2 = 2\,CaSO_4 + 2\,H_2O + SiF_4$$

consequently, $\dfrac{4\,F \cdot p \cdot 100}{SiF_4 \cdot a} = \dfrac{73.01\,p}{a}$ = per cent fluorine present.

Remark. — This method is suitable for the determination of fluorine in all fluorides that are decomposed by sulfuric acid. The analysis can be carried out in the presence of phosphates, but if carbonates are present they should be decomposed by ignition before the treatment with sulfuric acid. According to K. Daniel, exact results

* In routine work the determination of fluorine can be made without removing the last traces of silica with ammoniacal zincate solution. To apply the above procedure to the analysis of fluorite or other minerals containing little silica, about 0.6 g of pure silica should be added to 0.25 g of the sample before fusing with sodium carbonate at the start of the analysis.

are obtained only when the decomposition of the fluoride takes place at the temperature at which sulfuric acid boils. The method is not suitable for the determination of fluorine in topaz and micas.

Determination of Fluorine as Fluosilicic Acid, according to S. L. Penfield. Modified by Treadwell and Koch

Principle. — In this method the fluorine is expelled as silicon fluoride exactly as in the above method of Fresenius, but the gas is absorbed in 50 per cent alcoholic potassium chloride solution. By contact with water the silicon fluoride is decomposed into fluosilicic and silicic acids. The former unites with the potassium chloride, forming potassium fluosilicate, insoluble in 50 per cent alcohol:

$$3\,SiF_4 + 3\,H_2O \rightarrow 2\,H_2SiF_6 + H_2SiO_3 \qquad H_2SiF_6 + 2\,KCl = \mathbf{K_2SiF_6} + 2\,HCl$$

and sets free an equivalent amount of hydrochloric acid which can be titrated with 0.2 N sodium hydroxide solution, using cochineal as an indicator. From the above equations, it is evident that

$$1000 \text{ ml } 0.2\,N\text{ HCl} = \tfrac{3}{10} \text{ mole } CaF_2 = \tfrac{3}{5}\text{ F}$$
$$\therefore 1 \text{ ml } 0.2\,N\text{ NaOH} = 0.0234 \text{ g } CaF_2 \text{ or } 0.0114 \text{ g F}$$

Requirements. 1. *Pure Quartz Powder.* — Place pieces of pure rock crystal in a platinum crucible, heat strongly over the blast lamp, and then drop into cold water. After this treatment it is very easy to reduce the quartz to a fine powder by grinding in an agate mortar. Ignite the powder, and while still warm transfer to a flask fitted with ground-glass stopper. Allow the open flask and its contents to cool in a desiccator, stopper, and set aside.

2. *Sea Sand.* — Treat clean sea sand with boiling, concentrated sulfuric acid, wash, dry, ignite, and cool in a desiccator.

3. *Anhydrous Sulfuric Acid.* — Heat pure, concentrated sulfuric acid in a porcelain crucible until it is reduced one-third in volume and allow to cool in an empty desiccator.

Procedure. — Mix 0.1 g of the dry fluoride in an agate mortar, which is placed upon black glazed paper, with 2 g of the quartz powder, and transfer through the cylindrical arm A of the perfectly dry decomposition apparatus to the pear-shaped compartment B shown in Fig. 95. Then add 1.5–2 g of the sea sand, and mix with the rest of the material by shaking the apparatus. Then make connection with the dry U-tube, D, containing glass beads.* Place 15 ml of alcohol saturated with potassium chloride in each of the two Péligot tubes P and P_1. When the apparatus is connected as shown in the drawing, allow a dry current of air,† free from carbon dioxide, to enter at h, and pass through the apparatus at the rate of 2 or 3 bubbles per second. Then without stopping the air current, introduce about 20 ml of anhydrous sulfuric acid into the decomposition apparatus through the funnel T. By intro-

* This tube serves to keep back any sulfuric acid that is carried over mechanically.

† Wash the air by passing it through caustic potash solution, and dry it by passing through granular calcium chloride and concentrated sulfuric acid.

ducing the sulfuric acid in this way while maintaining the air current, the sulfuric acid and the greater part of the silica and fluoride mixture is made to pass directly into the compartment *B*. After adding the sulfuric acid, place the decomposition vessel in a paraffin-bath and heat slowly to a temperature of 130° to 140°. The evolution of silicon tetrafluoride at once begins, as is evident from the formation of foam. Continue passing air and heating the bath for 5 hours; then turn down the flame under the bath and pass air through the apparatus for half an

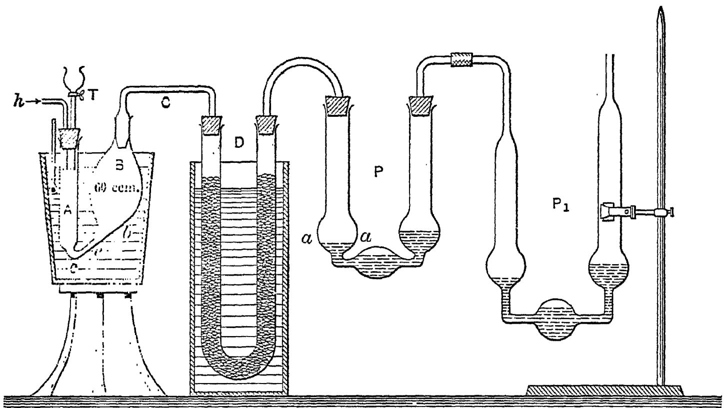

FIG. 95.

hour longer at the rate of 3–4 bubbles per second. During the heating the apparatus should be frequently shaken in order to bring the sulfuric acid into contact with all portions of the solid mixture. It is not necessary, however, with this arrangement of the apparatus, to shake as frequently as in the forms of apparatus described by Penfield and by Fresenius, because the air in its passage through the narrow connecting tube between *A* and *B* of the decomposition apparatus serves of itself to effect a good mixing. To accomplish this end, however, it is necessary to construct the apparatus exactly as shown in Fig. 95; the connecting tube between *A* and *B* must be so narrow that it is completely filled with the bubbles of air passing, and furthermore the parts marked *c e b* must form an inclined plane upon which the substance can readily pass back and forth. If there is a hollow in the apparatus at *c e b*, in which some of the substance can collect, the sulfuric acid may not come in contact with some of the fluoride so that the decomposition will be incomplete. Similarly it is necessary to guard against making the connecting tube *c e* too narrow, as otherwise the air will not pass in a uniform stream, but in spurts, so that in spite of the long tube *D* some

of the sulfuric acid fumes are likely to reach the Péligot tubes and thereby give rise to high results.

If not more than 0.1 g of the fluoride is present, the action is over at the end of $5\frac{1}{2}$ hours, and this is evident, as Daniel* was the first to discover, from the fact that the foaming in the apparatus ceases; the hydrochloric acid which has been set free in the Péligot tubes can now be titrated. To this end add a few drops of fresh cochineal† solution to each tube and titrate the contents with $0.2N$ potassium hydroxide solution with frequent shaking, until the indicator changes from yellow to red. This is, however, by no means the correct end point, because as Penfield observed, the gelatinous silicic acid encloses very appreciable amounts of hydrochloric acid. The silicic acid, therefore, must be thoroughly worked over with a stirring-rod and the addition of the alkali continued until the color change is permanent.

Remark. — This method is capable of giving excellent results but it is important that the apparatus and all the reagents added to the decomposition vessel should be perfectly dry. Phosphates do not interfere but carbonates must be removed by a preliminary ignition. If the mineral contains "combined water" there is danger of losing hydrofluoric acid by this ignition, but such loss can be prevented by adding an oxide such as lime or litharge.

The procedure can be modified to apply to the determination of fluoride in native sulfides such as sphalerite.‡ In this case mix 1 g of the substance (dried at 110°), with 2 g of sand and 2 g of anhydrous copper sulfate, and cover with 10 g of anhydrous chromic acid anhydride (CrO_3). After introducing sample and the sulfuric acid, as described above, gradually raise the temperature to 130–140° during 2 hours while passing a current of dry, CO_2-free air through the apparatus, and then heat 3 hours at this temperature.

In former editions of this book, it was proposed to dry the sulfuric acid over phosphorus pentoxide, but such acid evolves a little sulfuric anhydride in the analysis and the results are usually about 0.4 per cent too high.

Determination of Fluorine in Mineral Waters

Evaporate 1–10 l of the water (according to the amount of salts present) to a small volume, in a large dish, adding enough sodium carbonate to keep the solution slightly alkaline. Add an excess of calcium chloride, boil, filter off the precipitate and wash it with hot water until free from chlorides. Dry the precipitate, transfer it as completely as possible to a platinum dish, add the ash of the filter to the main precipitate, and gently ignite. This residue contains all the fluorine as calcium

* *Z. anorg. Chem.*, **38**, 257 (1904).

† Instead of cochineal, methyl orange may be used, although it is necessary then to add an equal volume of alcohol before titrating the hydrochloric acid.

‡ L. da Rocha-Schmidt and K. Krüger, *Z. anal. Chem.*, **63**, 29 (1923).

fluoride, besides considerable calcium (possibly strontium) and magnesium carbonates, iron, aluminum, and manganese oxides, often barium sulfate, and almost invariably some calcium phosphate. Moisten it with an excess of dilute acetic acid, allow to stand for some time with frequent stirring, and then evaporate to dryness on the water-bath. Treat this residue with water, filter, and wash with hot water. Transfer as much of it as possible to a platinum crucible, add the ash of the filter, and gently ignite the contents of the crucible. Mix 0.5–1 g of ignited quartz powder with the residue in an agate mortar. Transfer the mixture to the decomposition vessel *A*, Fig. 95, and treat with concentrated sulfuric acid exactly as described above by the method of Penfield. As only very little fluorine is present in this case, two small U-tubes can be used instead of the large Péligot tubes shown in Fig. 95.

Remark. — The formation of a precipitate in the first U-tube at the place marked *a a* in Fig. 95 indicates the presence of fluorine. It is well to confirm it by the etching test. After carrying out the titration of the hydrochloric acid set free, transfer the contents of the U-tube to a platinum dish, add a few drops of 2 *N* sodium carbonate, and evaporate the solution to dryness. Add ammoniacal zinc oxide (cf. p. 417), and again remove the liquid by evaporation. Take up the residue in water, and filter off the zinc oxide and silicate. Treat the filtrate with calcium chloride as described on p. 416, and apply the etching test.

Gas-Volumetric Determination of Fluorine according to Hempel and Oettel

See Part III, Gas Analysis.

Separation of Fluorine

(*a*) From the Metals

For the determination of the metals present, the fluorine usually can be removed by heating with concentrated sulfuric acid. However, with many silicates containing fluorine, *e.g.*, topaz, lepidolite, and other micas, this treatment will not accomplish the desired result. In such cases fuse the mineral with 4–6 times as much sodium-potassium carbonate, and remove the silica and aluminum as described on p. 417 by treatment with ammonium carbonate and ammoniacal zinc solution. Use the precipitates for the determination of aluminum and silica and the filtrate for the determination of the fluorine. The alkalies must be determined in a separate portion of the original substance (pp. 436, 437).

(*b*) Separation of Fluorine from the Acids

1. *Determination of Hydrochloric and Hydrofluoric Acids in the Presence of One Another*

With soluble alkali salts, precipitate the fluorine from the solution by means of a little sodium carbonate and an excess of calcium nitrate solution, as described on p. 416. Make the filtrate acid with nitric acid and determine the chlorine by precipitation with silver nitrate, according to p. 300.

It is simpler to treat the solution containing hydrochloric and hydrofluoric acids in a platinum evaporating dish with nitric acid and silver nitrate. Silver chloride is alone precipitated and can be filtered off, using a funnel of hard rubber, or a glass one coated over with wax. Wash the precipitate and weigh as described on p. 300. When phosphoric acid also is present, precipitate it with the chloride by the addition of silver nitrate to the slightly alkaline solution. Filter off the precipitate, wash with as little cold water as possible, and treat the precipitate with dilute nitric acid. By this means the silver phosphate goes into solution, while the silver chloride is unaffected. To determine the amount of phosphoric acid present, remove the silver from the solution by the addition of hydrochloric acid, and precipitate phosphoric acid in the filtrate by addition of magnesia mixture and ammonia (cf. p. 391).

In the filtrate from the silver phosphate and silver chloride precipitate, remove the excess of silver nitrate by the addition of sodium chloride and determine the fluorine as calcium fluoride.

In the case of an insoluble compound containing chlorine and fluorine, extract the melt obtained after fusing with sodium-potassium carbonate with water, remove the silica with ammonium carbonate and ammoniacal zinc solution as described on p. 417, and determine the chlorine and fluorine as above.

Usually it is more convenient to determine the two acids in separate portions of the substance.

2. *Determination of Boric and Hydrofluoric Acids*

To the solution containing the alkali salts of these two acids add an excess of calcium chloride at the boiling temperature. Filter off and wash with hot water.

Gently ignite the precipitate, consisting of calcium carbonate, calcium fluoride, and some calcium borate, treat with dilute acetic acid, evaporate to dryness, and add more acetic acid and water. By this means the calcium acetate and calcium borate go into solution, while

the calcium fluoride is left behind and can be determined as described on p. 416. For the boric acid determination take a second portion of the solution, make barely acid with acetic acid, and treat with a slight excess of calcium acetate solution to precipitate the fluorine. Place the solution, together with the calcium fluoride precipitate, in the Gooch retort and subject to distillation as described on p. 386.

FLUOSILICIC ACID, H_2SiF_6. Mol. Wt. 144.08

Forms: Calcium Fluoride, CaF_2; Potassium Fluosilicate; or volumetrically

1. Determination as Calcium Fluoride

Principle. — Alkali fluosilicates are decomposed on heating with sodium carbonate solution into fluoride and silicic acid:

$$Na_2SiF_6 + 2\ Na_2CO_3 + H_2O = 6\ NaF + H_2SiO_3 + 2\ CO_2$$

If a solution to be analyzed contains free fluosilicic acid or its sodium salt, add sodium carbonate solution until the reaction is alkaline and then considerable ammonium carbonate. Heat the solution to about 40°, and, after standing 12 hours, filter off the precipitated silicic acid.

The solution now contains all the fluorine as sodium fluoride, in the presence of small amounts of silicic acid, which can be precipitated by the addition of ammoniacal zinc solution (see p. 417). In the filtrate determine the fluorine as calcium fluoride, as described on p. 416.

Fuse an insoluble fluosilicate with 4 times as much sodium-potassium carbonate, extract the melt with water, and subject the solution to the above treatment.

2. Determination as Potassium Fluosilicate

This analysis is applicable only for the determination of free fluosilicic acid in aqueous solution.

Procedure. — Treat the solution with potassium chloride and an equal volume of absolute alcohol. Filter off the barely visible potassium fluosilicate through a tared filter which has been dried at 100°. After washing with 50 per cent alcohol dry the precipitate at 100° and weigh as K_2SiF_6.

The volumetric determination of fluosilicic acid will be discussed in Part II.

Analysis of Salts of Fluosilicic Acid

For the determination of the metal present, treat the salt with concentrated sulfuric acid in a platinum dish and heat until dense fumes of sulfuric anhydride are given off; silicon fluoride and hydrofluoric acid volatilize, while the metals are left behind as sulfates (cf. Vol. I).

*Determination of Water Present in Fluosilicates (Rose-Jannasch)**

The water cannot be determined by ignition, because all fluosilicates, even topaz, evolve silicon fluoride when subjected to this treatment (cf. Vol. I). If, as proposed by Rose, the substance is fused with 6 to 8 times as much lead oxide, all the water is evolved, while the fluorine remains behind:

$$R_2SiF_6 + 3\,PbO = 2\,RF + 2\,PbF_2 + PbSiO_3$$

The analysis is best performed according to the directions of Jannasch: Blow a bulb with a capacity of about 25 ml near one end of a tube of difficultly fusible glass which is 26 cm long and 1 cm wide. Near the middle of the longer side of the tube, between asbestos plugs, place a layer 3–5 cm long of pulverized, anhydrous lead oxide, and connect this end of the tube with two weighed calcium chloride tubes. Place the substance in the bulb, add 6–8 times as much lead oxide, and mix with the substance by carefully revolving the tube. Conduct a dry current of air through the apparatus and slowly melt the contents of the bulb. All the water and often some of the fluorine is thereby expelled, and the fluorine is absorbed by the layer of lead oxide. At the end of the operation cautiously heat this layer with a moving flame until no more water condenses in the cooler part of the tube. When all the water has been driven over into the calcium chloride tubes, weigh them with the customary precautions.

GROUP VII

SILICIC ACID (ALSO TANTALIC AND NIOBIC ACIDS)

SILICIC ACID, H_2SiO_3. Mol. Wt. 78.08

Form: Silicon Dioxide, SiO_2

Two cases must be considered:

(*a*) The silicate is decomposed by acids.

(*b*) The silicate is not decomposed by acids.

(*a*) Silicates Decomposed by Acids

Weigh out 0.5 g of the powdered silicate into a porcelain dish, add 25 ml of water, and stir till the silicate is thoroughly wet. Add in small portions, while heating the casserole and stirring, 25 ml of 6 *N* hydrochloric acid. Evaporate upon the water-bath with frequent stir-

* Rose-Finkener: *Lehrbuch der analyt. Ch.*, Vol. II, and Jannasch, *Praktischer Leitfaden der Gewichtsanalyse.*

ring until the residue is obtained in the form of a dry powder. In many cases the decomposition is shown to be complete by the fact that no gritty particles can be felt with the stirring-rod on the bottom of the dish. If, however, the substance contained quartz or some silicate that is not decomposed by hydrochloric acid, this is not the case and the procedure described on p. 430 should be followed. Heat the residue for at least an hour in the hot closet at 120–130°, to dehydrate the silica.

Moisten the dry powder with concentrated hydrochloric acid and allow the covered dish to stand for 10 minutes at the ordinary temperature, in order that basic salts and oxides formed during the evaporation and drying may be once more changed to chlorides. Then warm gently, dilute with 100 ml of water, heat to boiling, and, after the silicic acid has been allowed to settle, decant the clear liquid through a filter supported upon a platinum cone or a hardened filter placed in the apex of the funnel. Wash the residue 3 or 4 times by decantation, with hot $2N$ hydrochloric acid, then transfer to the filter and wash with hot water until free from chloride. Dry the precipitate by means of suction, place in a platinum crucible, and set aside for the time being. The separation of the silicic acid is not quite complete; as much as 2 mg may remain in the filtrate. To remove this, once more evaporate the solution to dryness on the water-bath, and again heat at 120–130°, for an hour, moisten the residue with 5 ml of concentrated hydrochloric acid, and allow to stand not more than 15 minutes.* Warm, dilute to 100 ml, boil and filter through a new and correspondingly small filter, washing with hot $2N$ acid and with water as before. Ignite the wet filters containing the silica in a platinum crucible. Keep the temperature low till all the carbon is consumed and do not allow the filter to catch fire. Finally cover the crucible and ignite over the blast lamp or over a Méker burner.

Remark. — It is not necessary to use suction in filtering. If the precipitate is allowed to dry before placing it with the filter in the crucible there is danger of losing some of the fine powder. The heating at 120° decreases the solubility of the silica in acid but this temperature should not be exceeded. Magnesia at a higher temperature recombines with silica and iron and aluminum oxides are formed in a condition hard to dissolve.

Testing the Purity of the Silica

The silica thus obtained is never absolutely pure, except in the analysis of a water-glass. Its purity must always be tested. For this pur-

* By being kept in contact with the acid for too long a time some silicic acid will go into solution.

pose cover it with 2 ml of water;* add a drop of concentrated sulfuric acid and about 5 ml of pure hydrofluoric acid. Place the crucible in an air-bath and evaporate under a good hood until no more vapors are expelled. Then remove the excess of sulfuric acid by heating over a free flame. Raise the temperature gradually and finally heat the crucible over a blast lamp or Méker burner, and again weigh. Repeat the treatment with sulfuric and hydrofluoric acids, without adding any more water, until the contents of the crucible (usually Al_2O_3, Fe_2O_3, TiO_2, ZrO_2, V_2O_5, P_2O_5, etc.) are at a constant weight. Deduct this amount from the weight of impure silica and add it to the precipitate obtained with ammonia in the subsequent analysis. The precipitate of Fe_2O_3, Al_2O_3, etc., should then be tested for SiO_2 by fusing the weighed precipitate with $KHSO_4$, treating the melt with dilute sulfuric acid, filtering, and testing the residue with hydrofluoric acid.

A great many silicates are incompletely decomposed, if at all, by direct treatment with hydrochloric acid in an open vessel. Inasmuch as it is necessary to test the purity of the silica by treatment with sulfuric and hydrofluoric acids, it might seem unnecessary to try to get a pure silicic acid residue before applying this treatment. Undecomposable silicates are likely to contain some alkali and alkaline-earth metal as well as iron and manganese in combination with silica. When such a silicate is treated with sulfuric and hydrofluoric acids, the alkali and alkaline earths are left as sulfates, the iron is left as Fe_2O_3, and the manganese as Mn_3O_4. Moreover, boron is volatilized as BF_3. Only when the silica is nearly pure and when the impurities are left as oxides in the same state of oxidation as at the start, and no other volatile constituent is present, does the loss in weight upon treatment with hydrofluoric and sulfuric acids represent the silicon content. If the silicate is only partly decomposed with acid it should be treated as an insoluble silicate.

(*b*) Silicates not Decomposed by Acids

Silicates not decomposed completely by the action of 6 N hydrochloric acid are usually fused with sodium carbonate which converts them partly into sodium silicate and partly into an ortho- or meta-silicate which can be decomposed with acid.

Jannasch† has decomposed refractory silicates by heating the finely ground powder in a 25-ml platinum tube with 10 N hydrochloric acid. On the end of the tube, a cap is fitted which is not quite air-tight. The platinum tube is placed in a larger glass tube which also contains a little hydrochloric acid. This tube is sealed and heated to 300–400° in a steel Mannesmann tube containing a little ether or petroleum ether to equalize the pressure. Owing to the high price of platinum and the fact that it is hard to get a perfect decomposition, this method of decomposition will never be popular although useful when only a little material is available for a complete analysis.

* If the water is not added, the mass will effervesce so strongly that there is danger of losing some of the impure silica.

† *Ber.*, **24**, 273 (1891); *Z. anorg. Chem.*, **6**, 72 (1894).

Jannasch and Heidenreich* have also recommended boric acid as a flux for decomposing silicates. To free the flux from alkali salts, the commercial acid should be recrystallized 2 or 3 times and heated in a large crucible to drive off all moisture, before powdering. This flux will decompose nearly all silicates. The very finely powdered mineral is heated over the blast lamp with 8 times as much or more of the flux. The contents of the crucible are cooled by means of cold water and the melt turned into an evaporating dish. By repeated evaporation with a saturated solution of hydrogen chloride gas in methyl alcohol, all the boric acid can be distilled off as methyl borate and the residue treated like that obtained after an ordinary decomposition with acid. Owing to the difficulty in getting thoroughly satisfactory fusions and trouble in removing the boric acid after the fusion, the method will never be a popular one although it permits the determination of alkalies in the same sample.

Jannasch has also recommended decomposition with lead oxide. The theory is similar to that of the dry assay for silver and gold. There the aim is to form a fusible slag with the silica and reduce the silver and gold to metal. Since the fusible slag is also decomposable with acid, it is clear that lead oxide is suitable when the determination of silica is desired. Moreover, the lead is easily removed so that alkalies can be determined in the same sample. On the other hand, if any free metal is formed, which will be the case if any precious metal is present, or if there is any reducing agent such as a few shreds of filter paper, or if a reducing flame comes in contact with the contents of the crucible, the crucible will alloy and be spoiled.

Fusion with Sodium Carbonate

Fuse 0.5 g of the very finely powdered substance in a platinum crucible with 3 g of sodium carbonate. The powdered silicate should be intimately mixed with the flux and a little sodium carbonate sprinkled on top. Heat the covered crucible at first over a small flame to drive out any moisture present. Gradually raise the temperature until finally the highest heat of a good Teclu or Méker burner is obtained. As soon as the mass melts quietly and there is no further evolution of carbon dioxide, the decomposition is complete. Wind a piece of platinum wire into a spiral and insert it into the fused mass. Remove the flame and allow the crucible to cool in the air somewhat and then play a stream of water upon the outside of the crucible. As soon as the crucible does not hiss when the water strikes it, quickly introduce enough water into the crucible to cover the melt. After about a minute carefully pull on the wire; usually the melt can be withdrawn from the crucible. If it does not come out easily, it can often be loosened by carefully heating the crucible.† Place the melt in a 300-ml

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it, together with its

casserole, add 25 ml of water, cover the casserole, and carefully add 25 ml of $6N$ hydrochloric acid. A lively evolution of carbon dioxide at once takes place, but as the silicic acid separates, the inner part of the cake gradually becomes coated with a film of silicic acid which protects it from the further action of the acid. Consequently it is necessary to break up the cake from time to time, by means of a glass rod, until finally there is no further evolution of gas and no more hard lumps remain. When manganese is present the melt is colored green with manganate and the solution is pink at first with permanganate but the latter gradually decomposes during the subsequent heating. After the evolution of carbon dioxide has nearly ceased, wash off the under side of the watch glass, raise it by placing a glass triangle under it, and evaporate to dryness. Heat the residue for at least an hour in the hot closet at 120–130°, to dehydrate the silica. Continue as described on p. 428.

Effect of Fluoride. — Substances containing considerable fluorine cannot be treated as above, for silicon fluoride will be lost by volatilization. Therefore it is necessary to use the old method of Berzelius. Extract the melt from the sodium carbonate fusion with water, as in the determination of fluorine (p. 417), and remove the greater part of the silica by means of ammonium carbonate. Filter off the precipitate, ignite, and weigh.

Precipitate the silicic acid remaining in the filtrate by means of ammoniacal zinc solution (p. 417). Dissolve this precipitate of zinc oxide and zinc silicate in hydrochloric acid and obtain the silica by evaporation on the water-bath as usual. As a rule, the insoluble part of the melt contains silicic acid, and this must also be removed by evaporation with hydrochloric acid. Ignite all three silica precipitates together and test the purity of the silica.

Analysis of Silicates

Orthoclase

Constituents: silicic acid (63–70 per cent); aluminum oxide (16–20 per cent); ferric oxide (0.3 per cent); potassium oxide (8–16 per cent); sodium oxide (1–6 per cent); and often small amounts of calcium oxide, magnesium oxide, and in rare cases barium and ferrous oxides.

Preparation of the Substance for Analysis

Break up large pieces of rock on a thick steel plate with a specially hardened surface and a similarly hardened pounder, such as street

pavers use. Place the small fragments in a "diamond" mortar or in one like that shown in Fig. 96. It is made of chilled and case-hardened tool steel. The dimensions of the block A are 12.5 by 12.5 by 6 cm and there is a depression in the center 0.6 cm deep. The pestle B is 20 cm high, and the diameter at the base is 3.5 cm. The cylinder C is 12.5 cm tall and of 5-cm outside diameter accurately fitting the depression in the block. Unlike the ordinary "diamond" mortar, the pestle has a smaller diameter than the inside diameter of the cylinder, which is 4.4 cm. The crushing is done with the pestle, without the aid of a hammer. With this mortar most of the sample can be reduced fine enough to pass through silk bolting-cloth.

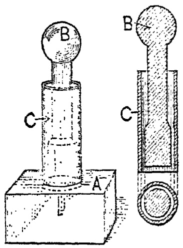

FIG. 96.

A finer powder can be obtained by hand grinding in an agate mortar but the McKenna ore grinder shown in Fig. 97 is more economical in the long run. A is a copper cup soldered to the head of the pestle holder and assumes, without friction, the motion of the latter. B is a tin plate with deep sinus and is covered by the rubber cloth C which fits closely about the metal shaft. These attachments A, B, and C prevent oil and dust from the belts and bearings from entering the mortar. The spring at the top of the sliding rod, to which the agate mortar is attached at the bottom, can be adjusted to give any desired pressure or can be thrown back to allow the pestle to be raised in removing the agate mortar. The pestle makes about 200 revolutions per minute and the mortar moves slowly in the same direction. The scraper keeps the material in the center, and the combined rolling and sliding motion reduces the hardest ore very quickly.

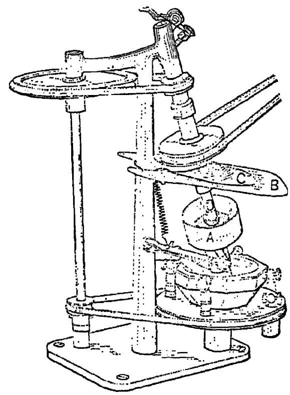

FIG. 97.

Do not attempt to grind too much at one time, and frequently sift through silk bolting-cloth to prevent as much as possible contaminating the sample by abrasion and loss of moisture by the heat of grinding. Prepare at least 5 times as much sample as is needed and make sure that all the powder is included; it is never admissible to take only the powder that passes through the sieve the first time. Mix well by rolling on a sheet of glazed paper, rubber, or oilcloth. A corner of the sheet is lifted and drawn across, low down, in such a way that the ma-

terial is made to roll over and over and does not merely slide along. The sample should be rolled back and forth along each diagonal for 100 times or more. Then the sample may be spread out into squares and a little taken from each square. Finally mix the sample chosen.

Weighing the Substance. — It has been customary to dry the powder at 100–110° until a constant weight is obtained. If there is danger of losing combined water by this procedure, it has been recommended to dry the powder in a vacuum over concentrated sulfuric acid. The practice of drying the substance in either of the above ways is, however, to be discountenanced. It is far better to use the air-dried substance for the analysis, and to determine the moisture in a separate sample. This is more accurate, because the dry silicate powder is hygroscopic, so that a portion weighed out today is likely to contain a different amount of moisture from one taken tomorrow, and this is not the case when the air-dried powder is taken for the analysis. Further, as Hillebrand had conclusively shown, chemically combined water is likely to be expelled not only by heating at 100° but also by drying in a vacuum over sulfuric acid. This is particularly true of the zeolites. In orthoclase, however, only about 0.1 per cent of moisture is present, so that in this particular case accurate results will be obtained by either method.

Determination of Silica, Aluminum, etc.

Weigh out 0.5 g of the air-dried substance in a spacious platinum crucible, dry for 1 hour at 105–7°, cool in a desiccator, and weigh. The difference in weight represents the amount of hygroscopic moisture.

Mix the dry substance with 3 g of calcined sodium carbonate by means of a platinum spatula, and determine silica as described on p. 430. Treat the silica with sulfuric and hydrofluoric acids, as described on p. 429, and set the crucible with the residue of Al_2O_3, etc., aside for the present.

Determination of Aluminum and Ferric Oxides

The filtrate from the silicic acid contains, besides the chlorides of aluminum, iron, calcium, and magnesium, a little platinum, from the crucible in which the fusion was made.

To remove the platinum, heat the solution to boiling and introduce hydrogen sulfide. Filter off the mixture of platinum sulfide and sulfur, and boil the solution to expel the excess of hydrogen sulfide. Oxidize the iron back to the ferric state by adding bromine water and boiling until the excess of the latter is expelled. After this add 10 ml of 2 N ammonium chloride solution and precipitate the aluminum, iron, etc.,

from the boiling-hot solution, by the addition of a slight excess of ammonia, free from carbonate (cf. p. 155). Allow the precipitate to settle, filter, and wash twice by decantation with hot water. Redissolve by running hot $2N$ hydrochloric acid through the filter into the beaker containing the greater part of the precipitate. Repeat the precipitation with ammonia as before, and after filtering and washing by decantation, transfer the precipitate to the filter and wash until free from chloride with water containing 2 per cent of ammonium nitrate. Allow the precipitate to drain as completely as possible, and ignite wet in the crucible containing the residue obtained from the treatment of the impure silica with sulfuric and hydrofluoric acids. After igniting strongly over a good Teclu or Méker burner weigh the crucible; its contents represent the sum of the aluminum and ferric oxides (also TiO_2, ZrO_2, P_2O_5, and V_2O_5, if present).

For the determination of the ferric oxide, fuse the mixed oxides with potassium pyrosulfate as described on p. 120. The decomposition is complete after 2–4 hours. Dissolve the melt in water containing a little sulfuric acid and determine the iron, after previous reduction with hydrogen sulfide (cf. p. 103), by titration with potassium permanganate (cf. p. 104). If the weight of the Fe_2O_3 is deducted from the weight of $Fe_2O_3 + Al_2O_3$, the weight of Al_2O_3 is obtained.*

Determination of Calcium

Evaporate the combined filtrates from the ammonia precipitate to a small volume, heat to boiling, and precipitate the calcium by means of a boiling solution of ammonium oxalate as described on p. 91. If the quantity of precipitate is small, ignite and weigh as CaO. If considerable calcium is present (cf. p. 90) redissolve the moist precipitate in hydrochloric acid, and repeat the precipitation by ammonia and a little more ammonium oxalate. Ignite strongly, and weigh as CaO. (Cf. p. 85.)

Testing of the Calcium Oxide Precipitate for Barium

Although it is usually unnecessary to make either a qualitative or quantitative test for barium in a sample of orthoclase, yet it is likely

* The amount of iron and aluminum can be determined more quickly, though less accurately, as follows: Dissolve the moist ammonia precipitate in hot, dilute sulfuric acid and dilute to a volume of exactly 250 ml. After thoroughly mixing, remove 100 ml by means of a pipet into a beaker and place a second portion of the same volume in a 200-ml flask. In the first portion determine the sum of Fe_2O_3 + Al_2O_3 by precipitating with ammonia, filtering, igniting, and weighing; in the other portion reduce the iron by hydrogen sulfide and titrate with permanganate.

to be present in traces so that it may be well to show how this can be done. As far as the author knows, strontium has never been found in orthoclase. On account of the solubility of barium oxalate in a solution of ammonium oxalate, the barium will rarely be found in the calcium precipitate when a double precipitation is made, except when it is present to an extent of more than 3 or 4 mg.*

To test a calcium precipitate for barium, dissolve it in nitric acid, evaporate to dryness, and heat for some time at 140°. Dissolve the calcium nitrate in ether-alcohol (p. 93, *a*), and examine any residue remaining behind in the spectroscope for barium. If barium is found, dissolve in dilute acid and repeat the precipitation with ammonia and ammonium oxalate. If no barium is found with the lime, it is by no means safe to conclude that barium is absent; it can very well have gone into the filtrate from the double precipitation of calcium. This amount will be precipitated with the magnesium as barium phosphate unless it is removed as indicated below.

For the quantitative determination of barium a separate portion of the substance should be taken (see below).

Determination of Magnesium

To the combined filtrates from the calcium oxalate precipitation, add a drop or two of sulfuric acid and allow the solution to stand 12 hours to see if any precipitate of barium sulfate will form. If it does, filter off the precipitate and test for barium according to Vol. I. In the filtrate from the barium sulfate determine magnesium as described on p. 80.

Determination of Barium

If the qualitative tests have shown the presence of barium, weigh out 2 g of the substance into a platinum dish; moisten with 10 ml of 7 *N* sulfuric acid and 5 ml of hydrofluoric acid. Evaporate the liquid on the water-bath, with frequent stirring, until the mineral is completely decomposed, when sandy particles will no longer be perceptible on stirring with a platinum spatula. Frequently a further addition of hydrofluoric acid is necessary. When the decomposition is complete, remove the greater part of the sulfuric acid by heating the contents of the dish in an air-bath. After cooling, take up the residue in water, filter off the barium sulfate, and ignite wet in a platinum crucible. The precipitate thus obtained always contains small amounts of calcium sulfate which must be eliminated. To accomplish this, dissolve the residue

* W. F. Hillebrand, *J. Am. Chem. Soc.*, **16**, 83 (1894).

in the crucible in a little hot concentrated sulfuric acid, and after cooling, dilute the solution with cold water. The barium sulfate is now completely free from calcium; filter, ignite again, and weigh.

Determination of the Alkalies

(a) *Method of J. Lawrence Smith**

Principle. — The substance is heated with a mixture of 1 part ammonium chloride and 8 parts calcium carbonate. By this means the alkalies are obtained in the form of chlorides, while the remaining metals are for the most part left behind as oxides (silicates and aluminates), and the silica is changed to calcium silicate, as represented by the following equations:

$$CaCO_3 + 2\ NH_4Cl \rightarrow CaCl_2 + 2\ NH_3 + H_2O + CO_2$$

$$2\ KAlSi_3O_8 + CaCl_2 + 6\ CaCO_3 \rightarrow 6\ CaSiO_3 + Ca(AlO_2)_2 + 2\ KCl + 6\ CO_2$$

The alkali chlorides together with the excess calcium chloride can be removed from the sintered mass by leaching with water, while the other constituents remain undissolved.

Preparation. — The ammonium chloride necessary for the determination is prepared by subliming the commercial salt; the calcium carbonate by dissolving the purest calcite obtainable in hydrochloric acid and precipitating with ammonia and ammonium carbonate. Carry out this last operation in a large porcelain dish. After the precipitate has settled, pour off the clear solution and wash the precipitate by decantation until free from chlorides. The product thus obtained contains traces of alkalies, but the amount present can be determined once for all by a blank test and a corresponding deduction made from the results of the analysis; it is usually sodium chloride and amounts to 0.0012–0.0016 g for 8 g calcium carbonate. The decomposition was performed by Smith in a finger-shaped crucible about 8 cm long and with a diameter of about 2 cm at the top and $1\frac{1}{2}$ cm at the bottom. Such a crucible is suitable for the decomposition of about 0.5 g of the mineral. A larger quantity can be analyzed in a somewhat wider crucible.

Filling the Crucible. — Mix 0.5 g of the mineral with an equal quantity of sublimed ammonium chloride by trituration in an agate mortar, add 3 g of calcium carbonate, and intimately mix again. Transfer the mixture to a platinum crucible with the help of a piece of glazed paper, rinse the mortar with 1 g of calcium carbonate, and add this to the contents of the crucible.

The Ignition. — Place the covered crucible in a slightly inclined position and heat gradually over a small flame until no more ammonia is evolved (this should take about 15 minutes). During this part of the operation the heat should be kept so low that ammonium chloride does not escape. The latter is dissociated into ammonia and hydrochloric acid by the heat, and the acid unites with the calcium carbonate to form calcium chloride. It is possible to decompose the silicate by

* *Am. J. Sci.* [2], **50**, 269, and *Ann. Chem. Pharm.*, **159**, 82 (1871).

using calcium chloride alone. Gradually raise the temperature until finally the lower three-fourths (and no more) of the crucible is brought to a dull red heat, and maintain this temperature for 50–60 minutes. Then allow the crucible to cool; the sintered cake usually can be removed by gently tapping the inverted crucible. Should this not be the case, digest a few minutes with water, which serves to soften the cake so that it can be readily washed into a large porcelain, or, better, platinum dish. Heat the covered dish with 50–75 ml of water for half an hour, replacing the water lost by evaporation and reducing the larger particles to a fine powder by rubbing with a pestle in the dish. Decant the clear solution through a filter and wash the residue 4 times by decantation, then transfer to the filter and wash with hot water until a few cubic centimeters of the washings give only a slight turbidity with silver nitrate. To make sure that the decomposition of the mineral has been complete, treat the residue with hydrochloric acid; it should decompose completely, leaving no trace of undecomposed mineral. The acid will usually gelatinize silica; the formation of a gelatinous precipitate does not indicate incomplete decomposition.

Precipitation of the Calcium. — To the aqueous solution add 50 ml of ammonium carbonate reagent, heat nearly to boiling, and filter. Evaporate the filtrate to dryness in a porcelain or platinum dish, heat the contents of the dish for an hour in a drying-oven at 110°, and remove ammonium salts by careful ignition over a moving flame. After cooling, dissolve the residue in a little water and remove the last traces of calcium by the addition of ammonia and ammonium oxalate to the hot solution. After standing 12 hours, filter off the calcium oxalate and receive the filtrate in a weighed platinum dish, evaporate to dryness, and gently ignite. After cooling, moisten the mass with hydrochloric acid to transform any carbonate into chloride, repeat the evaporation and ignition, and determine the weight of the dish and its contents; this shows the amount of alkali chloride present. Continue as on pp. 59–69.

(*b*) *The Hydrofluoric Acid Method of Berzelius*

Weigh 0.5 g of the powdered mineral into a platinum dish, moisten with 2 ml of water and 0.5 ml of concentrated sulfuric acid, mix with the substance by means of a platinum spatula, and after cooling add about 5 ml of pure, concentrated hydrofluoric acid. Evaporate the liquid on the water-bath, frequently stirring with the platinum spatula, until no more hydrofluoric acid is expelled and no more hard particles can be felt at the bottom of the dish.

Heat the dish in an air-bath until the greater part of the sulfuric acid is removed; this is necessary to make sure that the hydrofluoric

acid is completely expelled. It is not advisable, however, to remove all the sulfuric acid, on account of the danger of forming insoluble basic salts. Allow the mass to cool, cover with 200 ml of water, and digest until all the residue has gone into solution.* Transform the sulfates to chlorides by precipitation with as slight an excess of barium chloride as possible; and then, without stopping to filter off the barium sulfate, precipitate the aluminum, calcium, and excess of barium by the addition of ammonia and ammonium carbonate. Allow the precipitate to settle, wash 4 times by decantation, then transfer to the filter and wash free from chloride. Evaporate the filtrate to dryness, heat for an hour at 120°, and remove the ammonium salts by gentle ignition. Add a few drops of 6 N hydrochloric acid, and remove the magnesium by the Schaffgottsche method described on p. 84. In the filtrate determine sodium and potassium as described on pp. 59–65.

Remark. — This method is in very general use, and the results obtained agree closely with those by the J. Lawrence Smith method. Many silicates, such as the feldspars, are readily decomposed by the action of sulfuric and hydrofluoric acids;† others, such as certain specimens of tourmaline, only with difficulty. According to Jannasch the members of the andalusite group are not completely decomposed by hydrofluoric acid, but this can be effected by strongly igniting with ammonium fluoride. For this purpose place the ignited mineral in a platinum dish, cover with 10 ml of ammonia, evaporate to dryness, dilute with water, strongly acidify with concentrated hydrofluoric acid, and again evaporate to dryness. Place the dish in a nickel beaker and ignite quite strongly, until finally the excess of ammonium fluoride is driven off. Now treat the residue with 12 N sulfuric acid to decompose salts of fluosilicic acid, evaporate on the water-bath as far as possible, and remove then the greater part of the sulfuric acid by stronger ignition. From this point the procedure is the same as in the regular Berzelius method.

The Smith method is always applicable and has the advantage that the magnesium is practically completely removed at the start.

Analysis of Portland Cement

The American Society for Testing Materials has adopted a standard set of specifications‡ for portland cement, including its physical and chemical testing. The chemical methods recommended were those formulated by a committee who made a special study of this analysis. The following directions are based upon the report of the committee, but the procedure has been modified slightly in minor details and no attempt is made to reproduce the same wording. This scheme of analysis is given partly because of the technical importance of portland cement and partly because it has proved a satisfactory procedure to place in the hands of students as representative of a complete analysis.

* If barium was present, it is left behind as the sulfate.

† Many silicates can be decomposed by evaporation with hydrofluoric and hydrochloric acids. F. Hinden, *Z. anal. Chem.*, **1906**, 332.

‡ *Proc. Am. Soc. Testing Materials*, **12**, 301–28 (1912).

The mode of procedure adopted by the above-mentioned committee called for two evaporations for the removal of the silica. In the discussion of the method, however, it was pointed out that by heating the residue at 120°, not correcting for impurities by the hydrofluoric acid treatment and not correcting the subsequent precipitate formed by ammonia for small traces of silica, results are obtained which are within the permissible analytical error of the correct value. In fact, by this more rapid method, a compensation of errors takes place and the results are better in many cases than if the same operator attempted to carry out the analysis with the utmost precision possible.

The committee also recommended the use of platinum dishes and platinum crucibles as far as possible. The advantages gained are obvious, but the price of platinum has become so high that it is the duty of every practical chemist to avoid the use of platinum utensils wherever possible. The errors introduced by using porcelain instead of platinum are insignificant in most cases, although greater care must be taken to allow crucibles to cool before placing them in desiccators, and a longer time should elapse before weighing.

The original directions call for two precipitations of the calcium and for two precipitations of magnesium. This is unessential in the commercial testing of portland cement provided the conditions recommended are carefully fulfilled. The directions apply equally well to the analysis of limestone.

Procedure. — Weigh 0.5 g of limestone or cement into a 250-ml porcelain casserole, cover with 40 ml of water, and add 20 ml of $6N$ hydrochloric acid (*d.* 1.1), breaking up with a stirring-rod any lumps that form. Cover the casserole with a watch glass and digest about 15 minutes on a hot plate until the cement is decomposed completely. Rinse off the bottom of the cover glass with a little water and evaporate to dryness on the water-bath.* During the evaporation have the cover glass raised above the top of the casserole by means of a glass support. Heat the casserole and dry the residue in a hot closet at 120°.

Silica. — Moisten the residue with 10 ml of $6N$ hydrochloric acid, warm slightly, and add 150 ml of water. Cover the casserole with a watch glass and digest 10 minutes at a temperature near the boiling point. Filter into a 300-ml beaker; wash twice with $2N$ hydrochloric acid and then with hot water till free from chloride. Transfer the moist precipitate and filter to a weighed porcelain crucible with the paper folded so that the precipitate is entirely covered.† Smoke off the filter paper at a low heat without letting the paper take fire (cf. p. 428).

* At this temperature, the silicic acid becomes dehydrated so that it is practically insoluble in dilute acids. The presence of the calcium chloride from the cement helps the dehydration. The quantity of silica that passes into the filtrate is negligible and more than balanced by that obtained from the reagents and dishes. The residue should not be baked too hard. At higher temperature combination of basic magnesium salt and silicic acid takes place and alumina is made very insoluble.

† Dry silica is very pulverulent and easily lost if the gases from the paper escape too violently, as when it takes fire.

Finally ignite at the full heat of the Méker burner until a constant weight is obtained of a perfectly white precipitate. Report as "insoluble residue" in the analysis of limestone or as "silica" in the case of portland cement.

Precipitation of Iron and Aluminum. — To the filtrate and washings add 6 N ammonia solution until a slight ammoniacal odor persists after blowing away the vapors. Heat again just to boiling and promptly filter off the precipitate of $Fe(OH)_3$ and $Al(OH)_3$. Wash the precipitate 6 times with small portions of hot water. Reserve the filtrate for the calcium and magnesium determinations.

Sometimes the precipitate contains a little calcium carbonate from the carbon dioxide in the air and often a little magnesium hydroxide. Wash the precipitate back into the casserole, place the casserole under the funnel, pour 5 ml of hot, 3 N hydrochloric acid on the upper edge of the filter, and wash the filter with a little hot water. Continue the treatment with acid and water until all the precipitate left on the filter is dissolved. Finally wash the filter with a little dilute ammonia. Precipitate with ammonia just as before, filter through the original filter and wash this second precipitate till free from chloride. Ignite the second precipitate wet in a porcelain crucible and weigh as $Fe_2O_3 + Al_2O_3$, neglecting the small quantities of TiO_2, P_2O_5, and Mn_3O_4 which it may possibly contain. Unite the filtrate with that obtained from the first precipitate.

In the analysis of limestone, the weight of this precipitate will usually be small. The iron content will often arise from a little ferrous carbonate present in the sample. Disregard this fact and simply report the percentage of "combined oxides" present.

In the analysis of portland cement, the precipitate after ignition should be largely Al_2O_3, and it is customary to regard it as $Al_2O_3 +$ a little Fe_2O_3. The quantity of the latter should be determined by titration, as follows:

Ferric Oxide. — Transfer the ignited precipitate to a small beaker. Dissolve the traces that remain adhering to the crucible by heating small portions of 6 N hydrochloric acid in it, finally pouring each portion into the beaker. Use 20 ml of acid in all. Do not at any time dilute the hydrochloric acid until all the iron in the beaker is dissolved. Heat the acid with the iron and aluminum oxides at about 90° until all the iron has dissolved (cf. p. 116). When a clear solution is obtained, place the beaker on filter paper, reduce carefully with stannous chloride, and determine the iron content by the Zimmermann-Reinhardt process. Compute the percentage of Fe_2O_3 present and subtract this from the above weight of the oxides to get the per cent Al_2O_3.

Calcium Oxide. — Make the combined filtrates acid with acetic acid, bring to a volume of about 400 ml, heat to 80–90°, and slowly add, while stirring, 60 ml of hot, 0.5 N ammonium oxalate solution.* Add ammonium hydroxide until the solution is slightly ammoniacal and allow the precipitate to stand an hour, but not much longer, before filtering.

If considerable magnesium is present in the solution, some magnesium oxalate will come down with the calcium oxalate. If, therefore, more than 10 per cent of MgO is present in the substance analyzed, it is best to redissolve the calcium oxalate precipitate and repeat the precipitation. In this case, use a paper filter for filtering off the precipitate. When all the solution has passed through the filter, wash the precipitate with about 15 ml of hot water. Then rinse the precipitate back into the original beaker by holding the funnel in an inverted position and directing a stream of hot water against it. Replace the funnel in the support and wash the filter with about 25 ml of hot, 3 N hydrochloric acid. Heat the acid in a test-tube, pour it upon the upper edge of the paper, and catch the liquid as it runs through the filter in the beaker containing the precipitate. Finally wash the filter with a little hot water (and with dilute ammonia if it is to be used again for filtering the next precipitate). Heat the dilute acid in the beaker and add a little more acid if necessary to dissolve the precipitate completely. Dilute the solution to about 250 ml and repeat the precipitation of the oxalate at the boiling temperature, adding ammonia and 5 ml more of the ammonium oxalate reagent. Since the solution already contains oxalic acid equivalent to the calcium, only a little more reagent is necessary.

The calcium content of the precipitated calcium oxalate can be determined in various ways, all of which give good results.

(1) The filtered precipitate corresponds to the formula $CaC_2O_4 \cdot H_2O$. It can be weighed in this form without difficulty because the water of crystallization is retained even after long heating at temperatures considerably above the boiling point of water.

(2) It can be weighed as anhydrous calcium oxalate. To accomplish this it has been recommended to heat the precipitate to 200–300° for some time.

(3) It can be converted to calcium carbonate by heating to dull redness. The

$$CaC_2O_4 \rightarrow CaCO_3 + CO$$

takes place at about 400°, but Foote and Bradley† have shown that it is safe to heat at 675–800° if the precipitate is in a tubulated crucible and a current of CO_2 is constantly led through the crucible while it is being heated. The common way of accomplishing the decomposition is to heat for some time to dull redness, cool, moisten with a little ammonium carbonate reagent, and again heat carefully until

* About 10 g of NH_4Cl should be present in separating calcium and magnesium. This is usually present already at this stage in the analysis.

† *J. Am. Chem. Soc.*, **48**, 676 (1926).

no more odor of ammonia is perceptible. For the first heating, 2 hours in a muffle at 500° has been recommended, and after the treatment with ammonium carbonate solution, drying at 110° is sufficient.

(4) After the ignition to calcium carbonate, and it does no harm if some calcium oxide is formed, the precipitate can be dissolved in a measured volume of 0.5 N hydrochloric acid and the excess acid titrated with 0.5 N sodium hydroxide to a methyl orange end point.

(5) By strong ignition, calcium carbonate is changed to calcium oxide, which can be weighed. This method of handling the calcium oxalate precipitate is generally regarded as the best. Quantitative conversion can be accomplished in a covered platinum crucible by heating 1 hour with the full heat of a good Bunsen burner. The crucible should be covered loosely to prevent unnecessary loss of heat. A much shorter period of heating is necessary over a Méker burner or the blast lamp. A muffle heated to about 1000° can be used to advantage. The conversion of calcium oxalate to calcium oxide cannot be accomplished by heating in an open porcelain crucible over a Bunsen burner, and it requires a very long time to accomplish the conversion by heating in a covered porcelain crucible over a large Méker burner. The determination as oxide, therefore, is not to be recommended unless a muffle furnace or a platinum crucible is available.

(6) The original calcium oxalate precipitate can be dissolved in dilute acid and the liberated oxalic acid titrated with potassium permanganate solution. This is one of the most popular methods and gives good results. For this method of analysis, the precipitate should not contain over 0.1 g of calcium. In portland cement analysis, therefore, an aliquot of the filtrate from the iron and alumina precipitation should be taken or an aliquot of the solution of the calcium oxalate precipitate in acid. To take an aliquot of any solution, dilute it to a definite volume in a volumetric measuring-flask. After diluting to the mark, mix the solution by pouring it back and forth at least four times, using a beaker which is clean and dry at the start. Then, by means of a pipet or a smaller measuring-flask take out at once one or more fractional parts of the entire solution for further analysis. Thus the filtrate from the ammonia precipitation can be diluted to exactly 500 ml, the solution mixed and 50 ml (= one-tenth) taken for the calcium determination. The word *aliquot* in mathematics designates a number that will divide a larger number without leaving a remainder. In analytical chemistry it is used to represent an exact simple fraction of the whole sample taken for analysis.

Weighing as $CaC_2O_4 \cdot H_2O$. — Use a weighed Gooch crucible for collecting the calcium oxalate precipitate. The crucible can be weighed after drying at least an hour at 105–110° or after washing with alcohol and ether (cf. p. 81). Wash the precipitate with hot water until no chloride test is obtained on adding nitric acid and a little silver nitrate solution to the last portion of the filtrate, save the filtrate for the magnesium determination, and dry the precipitate by heating at 105–110° or by washing with alcohol and ether. The drying should take place in the same way both times. The precipitate contains 34.59 per cent CaO.

Weighing as CaO. — Use an ashless paper for collecting the precipitate. Wash the precipitate with hot water until free from chloride and save the filtrate for the magnesium determination. Transfer the

precipitate to a weighed platinum crucible. Ignite carefully with the flame at the mouth of the crucible until the precipitate is dry, and then heat with a small flame at the base of the crucible until all the paper is decomposed without letting it take fire. Then gradually raise the temperature and heat over a Tirrell burner for an hour with the crucible in an upright position and covered. Cool to about 100°, place in a desiccator, and weigh after 15 minutes. Repeat the heating until after cooling a constant weight is obtained. The calcium oxide is somewhat hygroscopic but is not difficult to weigh if it has been washed free from chloride. Call the weight constant if it agrees within 0.2 mg with the previous weight.

Titration with Permanganate. — Either a paper filter or a Gooch crucible can be used. After the precipitate has been washed free from chloride, transfer the precipitate together with the filter to a 400-ml beaker and dissolve the precipitate in 100 ml of warm 3 *N* sulfuric acid. Titrate at 70° with potassium permanganate as described on p. 102 for the standardization of permanganate against sodium oxalate.

Magnesium Oxide. — Make the filtrate acid with hydrochloric acid and concentrate to about 300 ml by evaporation on the hot plate. If the solution is accidentally evaporated to dryness, moisten the residue with 5 ml of 6 *N* hydrochloric acid and enough water to dissolve ammonium salts, which are always present when the magnesium is determined in the filtrate from the precipitation of calcium oxalate. If a clear solution is not obtained, heat to boiling and filter if necessary. Wash the precipitate (usually a little silica from the glass) once with 2 *N* hydrochloric acid and then with hot water till free from chloride.

To the acid solution, add an excess of diammonium or disodium phosphate — 1.2 g of $(NH_4)_2HPO_4$ or 3 g of $Na_2HPO_4 \cdot 12H_2O$ is ample — and some phenolphthalein indicator solution. Heat nearly to the boiling point and then slowly add 1.5 *N* ammonia water until a faint pink color is obtained and a slight precipitation takes place. Stir well for about a minute, touching the sides of the beaker as little as possible. When the precipitate has become distinctly crystalline, add more ammonia until a deep color is obtained with the phenolphthalein. Allow the solution to cool, then add one-fifth the solution's volume of concentrated ammonium hydroxide and allow to stand over night. (See p. 81.)

Sometimes no precipitation takes place on adding the amı will appear after standing over night in the presence of 2.5 *N* approximate concentration obtained by following the above directions. The reason for the tardy formation of a precipitate of magnesium ammonium phosphate is due to the retarding effect of the ammonium salts present. Sometimes, when the solu-

tion contains large quantities of ammonium oxalate, no precipitate appears. Three methods can be recommended for overcoming this difficulty. (1) Evaporate the solution to dryness in a porcelain casserole and heat the dry residue until no more vapors of ammonium salt are evolved. Cool, moisten the residue with 5 ml of 6 N hydrochloric acid, heat till basic salts are dissolved, dilute to about 25 ml, filter, and wash the filter with hot water until free from chloride. Add 5 ml of concentrated hydrochloric acid and some alkali phosphate if not already present. Dilute the solution to about 125 ml, heat nearly to boiling, and neutralize with ammonia as directed above. (2) Evaporate the solution to dryness after adding some nitric acid. To the residue add 25 ml of water, 50 ml of concentrated nitric acid, and 15 ml of concentrated hydrochloric acid, and again evaporate to dryness. By this treatment with aqua regia ammonium salts are oxidized to nitrogen. Finally treat this residue with 5 ml of 6 N HCl and 20 ml of water. Heat for a few minutes to dissolve basic salts and filter into a 250-ml beaker. Wash the filter with hot water till free from chloride, add 5 ml of concentrated hydrochloric acid, dilute to 125 ml, add 1.5 g of diammonium phosphate, and precipitate with ammonia as described above. (3) To the neutral solution add 5 g of sodium acetate and an excess of bromine water. Heat carefully and add more bromine until finally all the ammonium salt is oxidized. The reaction

$$C_2H_3O_2$$

will take place provided sufficient sodium acetate is present to keep the solution buffered.

Alkalies. — If it is desired to determine the alkalies the J. L. Smith method should be used (p. 436).

Loss on Ignition. — Heat 0.5 g of the cement for 5 minutes in a platinum crucible over a low flame, then heat strongly for 15 minutes.

Sulfuric Anhydride. — Fuse, in an iron crucible, 0.5 g of cement with 2 g of sodium peroxide and an equal weight of sodium carbonate, protecting the contents of the crucible from the flame as directed on p. 327. After the fusion, extract the soluble salts by treatment with hot water. Filter, make acid with hydrochloric acid, and evaporate to dryness on the steam-table. Moisten the residue with 5 ml of 6 N hydrochloric acid, dilute with 200 ml of water, and filter. Wash thoroughly and precipitate the sulfate in 400 ml of boiling solution by the addition of barium chloride (p. 328). Filter, ignite, and weigh. Report as percentage of SO_3.

Determination of Silicon in Iron and Steel

Silicon exists in cast irons and steels chiefly as a solid solution of Fe_2Si in iron. In wrought iron and in some steels, a little silicate of Fe or Mn may be present, such as $Mn_2Si_3O_8$; this really represents enclosed slag. The compound FeSi has also been identified in Fe-Si alloys. In cast irons, the silicon has a marked effect in causing the breaking down of cementite, Fe_3C, into Fe and graphite. With in-

creasing Si content, the graphite increases, but this effect is counterbalanced by the effect of S so that, roughly speaking, a given percentage of S neutralizes a definite percentage of Si.

Although Si enters into salts as silicate ion and not as Si^{++++} ions, the free element and its compounds with iron are oxidized very easily so that decomposition with any acid will cause oxidation of the Si to the quadrivalent state with evolution of hydrogen gas. There is, therefore, no loss of volatile silicon hydride when a sample of steel is dissolved in hydrochloric or sulfuric acid. If, however, nitric acid or other oxidant is used, the more powerful oxidizing agent is reduced without any evolution of hydrogen.

$$FeSi + 2\,H^+ + 3\,H_2O \rightarrow Fe^{++} + H_2SiO_3 + 3\,H_2\uparrow$$
$$Fe_2Si + 4\,H^+ + 3\,H_2O \rightarrow 2\,Fe^{++} + H_2SiO_3 + 4\,H_2\uparrow$$
$$3\,Fe_2Si + 28\,H^+ + 10\,NO_3^- \rightarrow 6\,Fe^{+++} + 10\,NO\uparrow + 3\,H_2SiO_3 + 11\,H_2O$$

In these reactions the product is really $SiO_2 \cdot xH_2O$ rather than exactly H_2SiO_3.

The following method* is excellent for the determination of silicon. Perchloric acid is used instead of sulfuric acid† because anhydrous perchlorates are easily soluble and there is no difficulty in dissolving the salts after the silica has been dehydrated. Chromium is oxidized to chromic acid and remains in solution. The chief precautions are to add sufficient perchloric acid to keep the mixture liquid after the nitric acid has been expelled and to *boil* at least 15 minutes at this stage in the analysis.

Procedure. — Treat 2.236 g of sample (5 times the factor weight) with 40 ml of $6\,N$ HNO_3 in a 400-ml covered beaker. When the sample is entirely decomposed, rinse and remove the watch glass cover and add 40 ml of 60–70 per cent $HClO_4$. Evaporate to fumes of $HClO_4$. Replace the watch glass on the beaker and heat so that the $HClO_4$ condenses and runs down the sides of the beaker for 15 minutes, but do not allow the contents of the vessel to become pasty or solid. Cool somewhat, and dilute with 125 ml of hot water. Stir until the salts have dissolved and crush any lumps with a glass stirring-rod. Filter and transfer all the residue to an ashless filter paper with the aid of $0.6\,N$ HCl, scrubbing the beaker with a rubber policeman. Wash alternately with 5-ml portions of hot $0.6\,N$ HCl and of hot water until all the iron salts have been removed. The washing must be done carefully as residual $HClO_4$ may cause loss of material in the subse-

* Willard and Cake, *J. Am. Chem. Soc.*, **42**, 2208 (1920).

† T. M. Drown, *Trans. Am. Inst. Mining Eng.*, **7**, 346 (1878–79).

quent ignition of the precipitate. Transfer the paper and residue to a weighed platinum crucible, and ignite slowly and carefully until all the carbon is gone. Cool in a desiccator, and weigh the *impure* SiO_2. Moisten the residue with $18\,N$ H_2SO_4 and add (without measuring) about 5 ml of HF. Heat inside an air-bath until all H_2SO_4 is expelled and then heat the crucible strongly over a free flame. Cool in a desiccator and weigh. The loss in weight represents the SiO_2, and, when the above weight of sample is taken, this loss multiplied by 20 gives the per cent of Si present.

Analysis of Lepidolite

Lepidolite is a member of the mica group and contains lithium and fluorine; the mineral has the following composition:

$$Si_3O_9Al_2(Li,K,Na)_2(F,OH)_2$$

SiO_2 = 40–45%;	Al_2O_3 = 19–38%;	MnO = 0–5%;
MgO = 0–0.5%;	K_2O = 4–11%;	Li_2O = 1–6%;
Na_2O = 0–2%;	F = 1–10%;	H_2O = 1–3%.

Besides the above, calcium, iron, phosphoric acid, and chlorine are frequently found, and in rare cases small amounts of cesium and rubidium are present.

The determination of the silicic acid, aluminum, iron, manganese, and magnesium is effected as in the orthoclase analysis, except that here the manganese must be separated from the iron and aluminum as described on pp. 158, 159, or 161.

Determination of the Alkalies. — Determine the weight of NaCl + KCl + LiCl by one of the methods given under the analysis of orthoclase, and weigh the potassium as potassium chloroplatinate. Then remove the platinum by treatment with hydrogen, or heat the solution to boiling and precipitate the platinum as sulfide by the introduction of hydrogen sulfide. Evaporate the filtrate to dryness and separate the lithium from the sodium as described on p. 69 or 70.

Determination of Fluorine. — This determination is the same as in the case of analysis of fluorine in calcium fluoride (p. 417), except that it is unnecessary to add any silica, for the mineral itself already contains a sufficient quantity.

Determination of Water. — This is effected by the method of Rose-Jannasch (p. 427).

Determination of Ferrous Iron in Silicates and Rocks

Weigh out 0.5–1.0 g of the powdered mineral into a platinum dish, cover with 5–10 ml of $7\,N$ sulfuric acid, and place upon the little tri-

angle (*a*) Fig. 98, made of glass or, better, platinum. Place this in the lead vessel *C* which rests in a paraffin-bath (*B*). After placing the cover upon *C*, pass a rapid current of carbon dioxide through *A*, whereby the air within the apparatus will be replaced in about 3 minutes. Quickly remove the cover, and add 5–10 ml of concentrated hydrofluoric acid. At once replace the cover, and continue the stream of carbon dioxide, while stirring the contents of the dish repeatedly during the whole operation by means of a platinum spatula or piece of coarse wire introduced through the other hole in the cover (in the drawing this opening is placed too far to the right). At the same time heat the paraffin-bath to 100° and keep at this temperature for about an hour. As soon as no more gritty particles are to be felt, raise the temperature of the bath to about 120° to remove the large excess of hydrofluoric acid. This requires about another hour. Allow the dish to cool in the carbon dioxide atmosphere, and finally wash its contents into 400 ml of cold distilled water. Add 10 ml of concentrated sulfuric acid and titrate the solution with standard potassium permanganate solution until a pink color is obtained which is permanent for several seconds. This end point is fugitive in proportion to the amount of hydrofluoric acid remaining in the solution.

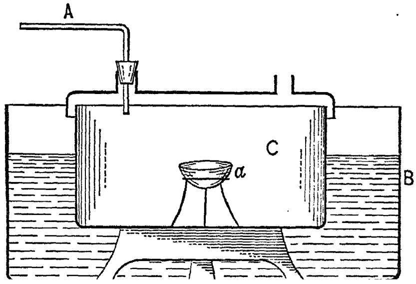

FIG. 98.

Remark. — The above method has been used in the author's laboratory with success for several years. It is a modification of Cooke's* method in which the decomposition with hydrofluoric acid took place under a glass funnel upon the water-bath. In this case a large amount of hydrofluoric acid remains in solution and it is difficult to obtain a sharp end point.

W. F. Hillebrand,† of the U. S. Bureau of Standards, prefers the

Modified Pratt Method

Place 0.5–1.0 g of the fine powder in an 80–100 ml platinum crucible, cover with water and add 10 ml of $9N$ sulfuric acid, cautiously if any carbonate is present. Add air-free hot water till the crucible is nearly half full. Place the crucible, with its cover on, on a triangle near a very low flame protected from drafts. Displace the air in the cru-

* *Am. J. Sci.* [2], **44**, 347 (1867).
† U. S. Geol. Survey, *Bull.* 700.

cible by introducing a stream of carbon dioxide through a small tube placed under the cover of the crucible. In a short time the liquid in the crucible boils but before this happens stop the current of gas and drop the crucible cover in place. From a small platinum crucible held in one hand, while the other draws the crucible cover to one side, add 5–7 ml of hydrofluoric acid. Quickly replace the lid and increase the heat but take care not to let the liquid boil over. As soon as steam issues, lower the flame and keep so that there is steady boiling without danger of loss for about 10 minutes. Then transfer the crucible, without removing the cover, to 200 ml of cold, saturated boric acid solution. Remove the crucible with a stirring-rod, rinse it out and titrate at once with permanganate, added rapidly until the first pink blush appears throughout the whole liquid.

If an unattacked residue remains in the beaker, filter it off and repeat the above treatment.

Another method for the determination of the amount of ferrous iron present in insoluble silicates is that of Mitscherlich. The silicate is decomposed in a closed tube with sulfuric acid ($8H_2SO_4{:}1H_2O$) under pressure, and the resulting solution titrated with potassium permanganate. This method usually gives good results in the case of a silicate analysis, but it is worthless for the analysis of rocks containing pyrite or other sulfides, which on treatment with sulfuric acid are decomposed.* The sulfur serves to reduce iron that was originally present in the ferric form, so that a high result is obtained.

Separation of Soluble from Insoluble Silicic Acid: Lunge and Millberg†

Frequently a mixture of silicates is to be analyzed which is partly decomposed on treatment with acids, with the separation of gelatinous silicic acid, and partly unaffected. The silicic acid deposited from solution by the addition of acids is soluble in 5 per cent sodium carbonate solution, while quartz and feldspar are not appreciably attacked by the latter (cf. Vol. I).

If it is desired to separate the deposited silicic acid from the unattached silicate (usually feldspar and quartz), treat the substance with acid (hydrochloric or nitric) and evaporate on the water-bath until a dry powder is obtained. Moisten this with acid, dilute, boil, and filter. After washing, digest the residue with 5 per cent sodium carbonate solution on the water-bath, in a porcelain dish for 15 minutes. Filter; wash the residue first with soda solution and finally with water.

* L. L. de Koninck, *Z. anorg. Chem.*, **26**, 125 (1901), Hillebrand and Stokes, *J. Am. Chem. Soc.*, **22**, 625 (1900), Stokes, *Am. J. Sci.*, Dec., 1901.

† *Z. angew. Chem.*, **1897**, 393, 425.

The alkaline filtrate contains the soluble silicic acid; this can be determined by acidifying and evaporating to dryness. The residue from the sodium carbonate treatment, consisting of quartz and feldspar, is weighed. To determine the quartz, treat with sulfuric and hydrofluoric acids, remove the excess of the HF by heating to fumes of sulfuric acid, and dissolve the cold residue in water. In this solution precipitate the alumina, as described on p. 95, and weigh the Al_2O_3. If this weight is multiplied by 5.41, the corresponding amount of feldspar is obtained; and if this is deducted from the weight of the quartz + feldspar, the weight of the quartz will be found.

Determination of Soluble Silicic Acid in Clay

Clay contains besides alumina, sand (quartz + breccia), and small amounts of calcium and magnesium carbonates.

Moisten 2 g of the coarsely powdered substance, which has been dried at 120°, with water, and add 150 ml of 12 N sulfuric acid.* Cover the porcelain dish with a watch glass and heat over a free flame until dense fumes of sulfuric acid vapors are evolved. Allow the contents of the dish to cool, add 150 ml of water and 3 ml of concentrated hydrochloric acid, boil for 15 minutes, filter, wash completely, and treat the mixture of soluble silicic acid, quartz and insoluble silicate as above.

Remark. — It was formerly the custom to separate the soluble silica from the insoluble silica by boiling with potassium hydroxide solution. According to the experiments of Lunge and Millberg, however, this is not permissible because quartz is appreciably soluble in caustic potash solution. If, on the other hand, the substance is obtained in a very finely divided condition, even sodium carbonate solution cannot be used for the same reason.

Analysis of Zircon†

Zirconium occurs widely disseminated in small quantities as the refractory silicate zircon, $ZrSiO_4$. In the simple process given below, the mineral is decomposed by two successive fusions and the zirconia is precipitated by hydrolysis with thiosulfate.

Lundell and Knowles‡ have described a more elaborate process, involving cupferron precipitation, and applicable to more complex mineral mixtures.

Procedure. — Reduce the mineral to an impalpable powder, weigh out about 0.5 g in a tared platinum crucible, and heat strongly to determine *loss on ignition.*

Fuse the calcined mass with about 5 g of sodium carbonate in the covered platinum crucible over the full flame of a Teclu burner for an hour. Digest the cooled melt with hot water, filter into a porcelain

* Alexander Subech, *Chem. Ind.*, **1902**, 17.

† Powell and Schoeller, *Analyst.*, **44**, 397 (1919).

‡ *J. Am. Chem. Soc.*, **42**, 1439 (1920).

casserole, and wash the residue well with hot water. Call this residue *A*. To the aqueous extract from the sodium carbonate fusion, add an excess of HCl, evaporate, and dehydrate the silica as described on p. 428. Filter off the silicious residue, and call this *B* and the filtrate *C*.

Fuse *A* with $KHSO_4$ (p. 120), and digest the melt with 100 ml of hot *N* H_2SO_4. Filter off any undissolved residue, and combine the filtrate with *C*.

Ignite this last residue together with *B* in a tared platinum crucible; determine its weight. Treat with H_2SO_4 and HF to determine the SiO_2 present (p. 428). Fuse the residue from this treatment with $KHSO_4$, leach with 1 per cent H_2SO_4, and add the solution to *C*. After this last fusion, everything except SiO_2 should have been dissolved and be present in *C*.

Neutralize the acid with $NaHCO_3$ until a slight permanent precipitate is formed. Dissolve this by adding a few drops of dilute H_2SO_4. Add a little ashless filter pulp (p. 98), and saturate the solution with H_2S at 50°. Filter, and wash the precipitate with hot water containing a little NaCl. Discard this precipitate of PtS_2 and S; the purpose of the H_2S treatment was to remove platinum that was introduced into the solution from the crucibles used in the fusions and to reduce the ferric iron to the ferrous condition. Nearly neutralize the filtrate with fresh Na_2CO_3 solution, but stop before there is any permanent darkening due to FeS. Boil in a current of CO_2 to expel H_2S.

To the hot solution add 10 g of $Na_2S_2O_3 \cdot 5H_2O$ dissolved in 20 ml of water and continue boiling for an hour, replacing water lost by evaporation. Add filter-paper pulp (p. 98), filter, and wash the precipitate on a paper filter 15 times with hot water. Call the filtrate *D*.

The precipitate contains ZrO_2, (HfO_2) and possibly some Al_2O_3 and TiO_2. Ignite it in a tared platinum crucible, and digest the oxides with hot *N* HCl; make ammoniacal and again filter, but wash the residue this time with dilute ammonium nitrate solution (p. 95). Add the filtrate to *D*. Ignite the residue to constant weight and weigh as ZrO_2(+ HfO_2 and possibly a little Al_2O_3 and TiO_2). To determine the Al and Ti in this precipitate, fuse it with 5 to 10 g of Na_2CO_3 for 2 hours in a platinum crucible over a Teclu burner. Leach the melt with hot water, and determine the Al in the filtrate (which dissolves as sodium aluminate) by making acid and proceeding as described on p. 95. Fuse the ignited residue from this last Na_2CO_3 fusion with $KHSO_4$ and determine the Ti colorimetrically (p. 106).

Any iron present in the mineral is contained in the filtrate *D*. Boil with a little Na_2CO_3 and Br_2, and filter off the precipitate. Dissolve it in dilute HCl, reprecipitate with NH_4OH, ignite, and weigh as Fe_2O_3.

Analysis of Chromite

Although chromite (chrome iron ore) is not a silicate, it is insoluble in all acids, and can be brought into solution by fusion with alkali carbonates, or borates, so that its analysis will be discussed at this place.

Chromite contains 18–39 per cent FeO, 0–18 per cent MgO, 42–64 per cent Cr_2O_3, 0–13 per cent Al_2O_3, and 0–11 per cent SiO_2. Calcium, manganese, and nickel are also occasionally present.

Of the finely powdered and bolted mineral, fuse 0.5 g in an inclined, open platinum crucible with 4 g of pure sodium carbonate* for 2 hours over a good Teclu or Méker burner. After cooling, leach the melt with water, acidify with hydrochloric acid,† evaporate in a porcelain dish until a dry powder is obtained, moisten with hydrochloric acid, take up in water, and filter off the silica. Ignite, weigh, and test the purity with hydrofluoric acid (p. 428). Introduce hydrogen sulfide into the hot filtrate from the silicic acid and filter off the precipitate of platinum sulfide and sulfur. Catch the filtrate in an Erlenmeyer flask, add 10 ml of ammonium chloride, enough ammonia (free from carbonate) to make the solution alkaline, and a little freshly prepared ammonium sulfide. Stopper the flask and allow the contents to stand over night. In the morning filter off the precipitate, wash twice with water containing a little ammonium sulfide, dissolve it in hydrochloric acid, and repeat the precipitation with ammonium sulfide. Determine calcium and magnesium in the filtrate as described on p. 90.

Dissolve the ammonium sulfide precipitate in cold $2N$ hydrochloric acid, filter off any residue of nickel or cobalt sulfide, and dry. Ignite this residue first in air, then in a current of hydrogen, and finally weigh as metal. It is not worth while to attempt the separation of the nickel from the cobalt on account of the small amount present. Expel hydrogen sulfide from the filtrate from the sulfides of nickel and cobalt by boiling, oxidize the iron present by adding bromine and separate the iron, chromium, and aluminum from the manganese by means of the barium carbonate method (p. 156) and from one another as described on pp. 113 *et seq.* In the filtrate from the barium carbonate precipitate, separate the manganese from the barium as described on p. 135, *b*, and determine as sulfide or as sulfate.

Remark. — If it is desired to determine the chromium alone, this is best accomplished by means of a volumetric process (see Part II).

* Bunsen fused the chromite with one-third as much SiO_2 and 6–8 parts : and then subtracted the amount of silica added from the total amount found. This makes the decomposition take place more readily, but the author prefers not to add the silica on account of the possibility of thereby introducing an error.

† If a dark residue of undecomposed mineral should remain, filter it off and again fuse with sodium carbonate.

Determination of Thorium in Monazite*

(a) Separation of Thorium and Cerium by Sodium Thiosulfate

Monazite is a phosphate of the rare earths [(Ce,La,Di,Th)PO_4]. It occurs in so-called " monazite sand " mixed with quartz, rutile, zircon, tantalates, etc., and has been used as raw material for the preparation of thoria (used in the Welsbach mantle). The value of a sample of monazite sand depends upon the amount of thorium present, and its determination is best accomplished as follows:

Digest 50 g of monazite sand in a porcelain dish with 100 ml of concentrated sulfuric acid for about 5 hours, or until no yellow, undecomposed grains remain. This treatment easily dissolves all the thoria, which determines the value of the sand, but does not dissolve much ilmenite. It is advantageous not to get all the TiO_2 into solution as this will interfere with subsequent work. Cool, and mix slowly with 500 ml of ice-cold water contained in a liter measuring-flask. Allow to stand over night.

In the morning, make up to the mark, mix, and filter. Use 100 ml of the filtrate for the subsequent analysis. If metals of the copper-tin group are present, saturate the solution with hydrogen sulfide, filter, wash, and heat the filtrate to expel the excess hydrogen sulfide. Add NH_4OH and NH_4Cl to precipitate the rare earths with the iron-aluminum group. Filter and wash the precipitate.

Dissolve the precipitate in dilute hydrochloric acid,† adjusting the acidity so that approximately 0.1 g of rare-earth oxide is present in 60 ml of solution which is not over 0.5 N in hydrochloric acid. Heat the solution to 60°, and precipitate the rare-earth oxalates by the addition of sufficient oxalic acid to leave about 3 g of the crystals in 100 cc of the final solution. Allow the solution to stand at 60° for some time, preferably over night. (If considerable titanium or zirconium is present, it is best to ignite the precipitated oxalates, dissolve in hydrochloric acid, and repeat the precipitation with oxalic acid.) Filter off the oxalate precipitate; wash thoroughly with hot water containing a little hydrochloric and oxalic acids.

Ignite the rare-earth oxalates to form the oxides. Dissolve the oxides in hot hydrochloric acid, and evaporate the solution to dryness on the water-bath. Moisten the residue with 5 ml of water and again dry. Then add 200 cc of water and 9 g of sodium thiosulfate crystals dissolved in 30 ml of water. Allow to stand over night. In the morning, boil the solution for 10 minutes and filter off the precipitate of $Th(OH)_4$ and sulfur. Wash with hot water and boil the filtrate vigorously for an hour to see if there is any further precipitation. If so, filter through a fresh filter, wash thoroughly, and set this precipitate aside.

Wash the main precipitate back into the original beaker with as little water as possible, boil with 10 ml of concentrated hydrochloric acid, and filter into a small evaporating dish, washing the sulfur precipitate well. Evaporate the filtrate to dryness, and repeat the entire treatment with water and sodium thiosulfate, using 150 ml of water and only 3 g of sodium thiosulfate dissolved in a little water. Finally make a third precipitation in the same way.

* U. S. Bur. Mines., *Bull.* 212.

† The directions here given originated with Schoeller and Powell, *Analysis of Minerals and Ores of the Rarer Elements* (1919).

Test the filtrates from the second and third thiosulfate precipitations by adding ammonia; if any considerable precipitation takes place the thiosulfate precipitation must be repeated.

Dissolve the final precipitate of thorium hydroxide in 20 ml of 6 *N* hydrochloric acid, dilute the solution to 150 ml, heat to 60°, and add 30 ml of cold, saturated oxalic acid solution. Allow to stand half an hour, then stir vigorously and allow to stand at least 4 hours at 60°. Filter; wash with hot, very dilute hydrochloric and oxalic acid solution. Ignite the thorium oxalate, and weigh as ThO_2.

Take the precipitate produced by 1 hour's boiling of the filtrate from the first thiosulfate precipitation, the ammonia precipitates after the second and third precipitations, together with the sulfur residues, and ignite. Fuse with potassium pyrosulfate, cool, leach with hot water, precipitate with ammonia, dissolve in hydrochloric acid, evaporate to dryness, and carry out the thiosulfate precipitation as above. Add the small quantity of ThO_2 obtained after the final precipitation as oxalate to that originally obtained.

*Notes:** — 1. The rare-earth oxides rarely dissolve perfectly in hydrochloric acid. When no more seems to dissolve, add a little potassium iodide and reheat. Boil off most of the iodine and oxidize the remainder with a little sulfurous acid and filter until a clear filtrate is obtained.

2. If the initial separation of the rare earths as oxalates has been properly performed so that only traces of phosphate are contained in the precipitate, then if the final thiosulfate precipitate is washed and ignited to oxide it will only be about 0.2 per cent too heavy.

3. When extreme accuracy is not necessary, the filtrate from the first oxalate precipitation, and the filtrate from the three thiosulfate precipitates can be neglected and the last thiosulfate precipitate ignited and weighed.

(*b*) *Separation of Cerium and Thorium by Potassium Iodate*†

The thiosulfate method is long and tedious. The iodate method is much more rapid and gives results which are nearly, if not quite, as good.

Treat 50 g of monazite sand with sulfuric acid, as described above, and use one-
of the diluted solution. To the 50 ml aliquot, add 50 ml of concentrated nitric
and cool. Add a solution of 15 g of potassium iodate in 30 ml of water and 50
... half an hour with frequent
stirring.

Wash the precipitate back into the beaker and cover with 200 ml of a solution con-
... nitric acid per liter. Again pour

the beaker again, heat to boiling, and dissolve the

of potassium iodate dissolved in a little concentrated nitric acid and water.

To remove titanium and zirconium, dissolve the precipitate in hydrochloric acid and a little sulfurous acid to reduce any cerium to the cerous condition, make slightly basic with ammonia, and filter. Wash the precipitate free from iodide, dissolve again in hydrochloric acid, and precipitate the thorium as oxalate by means of a large excess of oxalic acid as in the preceding method. Ignite and weigh as ThO_2.

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* These notes were very kindly furnished by H. F. V. Little of Thorium, Ltd.,

Speter, *Chem. Ztg.*, **34**, 306 (1910); Schoeller and Powell, *loc. cit.*

Water in Silicates

The total hydrogen content of any substance can be determined under suitable conditions as water. Hillebrand* has classified the condition of hydrogen in minerals as follows:

A. Essential hydrogen representing a part of the characteristic molecular or crystalline structure.

I. Present in definite stoichiometric proportions.

(*a*) As acidic or basic hydrogen (*e.g.*, $KH_2Al_3(SiO_4)_3$) †

(*b*) As water of crystallization.

II. Not present in stoichiometric relations with reference to the substance as a whole but present in one of the above forms in some constituent, the entire substance being a solid solution or isomorphous mixture of two or more individuals.

B. Non-essential hydrogen, not necessary for the characterization of the mineral.

I. In liquid solution, as in deliquescent powders or in amorphous material including supercooled liquids.

II. Held by surface forces.

(*a*) Adsorbed in films of molecular thickness.

1. On walls of cavities within grains of aggregates.
2. On the exteriors of grains.

(*b*) Held by capillarity, in liquid form.

1. In colloids with mesh structure.
2. In definite openings within aggregates.
3. In spaces between grains.

III. Included hydrogen.

(*a*) As liquid droplets in cavities.

(*b*) As included grains of other minerals.

There is no rule to lay down to enable the chemist to differentiate between these different classes.

* U. S. Geol. Survey, *Bull.* 700.

† Inasmuch as hydrated alumina does not ionize appreciably as either an acid or a base, and the above formula can be rewritten to make the hydrogen appear basic $KAlO(AlOH)_2(SiO_3)_3$, and the mineral a meta instead of an ortho silicate, it is idle to spend much time arguing whether the hydrogen in such a mineral is really acidic as the first formula indicates or possibly basic as the second formula shows.

If the mineral on ignition loses nothing but water, the amount of the water can be determined by the loss in weight. Usually, however, other constituents (*e.g.*, CO_2, SO_2, Cl, F, etc.) are lost, and the substance may undergo an oxidation (FeO is changed to Fe_2O_3; PbS to $PbSO_4$, etc.). In such cases the procedure recommended by Jannasch can be used to advantage. The substance is heated with lead oxide, and the water vapor is conducted over a heated mixture of lead oxide and lead peroxide and absorbed in a weighed calcium chloride tube (see p. 427).

If the substance on ignition loses simply water and carbon dioxide the water may be accurately determined by the method of Brush and Penfield.*

Brush and Penfield's Method

The rock powder is heated in a hard glass tube, closed at one end, containing one or more enlargements to provide for the condensation of the water. For most purposes, the tube *a* shown in Fig. 99 is satisfactory. It is 20–25 cm long and has an internal bore of about 6 mm. If the water is expelled with difficulty, the tubes

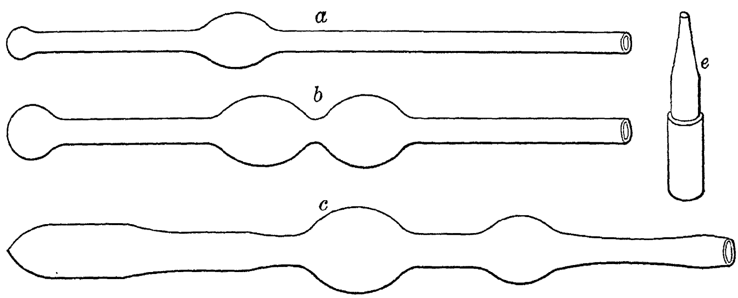


Fig. 99.

b and *c* are sometimes preferred. The tube *d* is a thistle tube used for introducing the powder into the tube and *e* is a tip which is placed on the open end of the tube during the heating to prevent diffusion of air in and out of the tube. At the start and finish, it is important that the tube should be dry on the inside. To dry the tube, insert a piece of glass tubing, extending to the bottom of the tube, and connect the outer end with the suction pump. In weighing the tube, a brass tube support should be used for holding it on the balance pan.

First weigh the tube and its brass support. Then introduce about 1 g of the rock powder through the thistle tube, which must be dry on the inside. A suitable filling tube can be made from a 5-cc pipet,

* *Am. J. Sci.* [3], **48**, 31 (1894), and *Z. anorg. Chem.*, **7**, 22 (1894); Washington, *The Chemical Analysis of Rocks.*

cutting the bulb in two and reducing the length to 25 cm. After the tube is filled weigh the tube and brass support again to find the weight of powder taken. Avoid rolling any of the powder toward the open end.

Clamp the tube in a horizontal position, and tap it gently to afford a free passage for the heated air above the powder and connect the tip *e* with the open end of the tube. Place a narrow strip of filter paper or lamp wicking around the bulb and the farther end of the tube, with the ends dipping in cold water. This is to keep the walls of the tube cold so that water will condense but the wicks should not be so near the open end that there is any chance of water getting into the tube from the outside.

Carefully heat the closed end of the tube, gradually increasing the heat until the full heat of a Tirrill burner is obtained. With some minerals the heat of the Méker burner is necessary. If the end of the tube tends to sink, gently turn it around from time to time.

After the powder has been well ignited, and the water completely expelled, which will take at least 15 minutes, seal a short piece of narrow glass tubing to the hot end of the tube where the substance lies, to serve as a handle. Lower the flame and cautiously drive any condensed moisture near the substance into the bulb, taking care not to crack the tube. When this is accomplished and there are no longer any drops of water near the substance, soften the hot end by heating with the tip of a Méker burner. When the tube is sufficiently soft all around, draw off the end containing the powder and seal the tube without allowing the flame to enter.

Allow the tube to cool in a horizontal position, wipe dry on the outside, and weigh after it has reached room temperature, removing the tip while weighing. It is well to test the condensed water with litmus to see if it is acid or basic. After the tube has been weighed, dry with suction as at the beginning before the first weighing. Cool, wipe dry on the outside, and weigh again. The difference between the last two weights is the amount of *total* water contained in the rock powder.

If the rock contains minerals like talc, topaz, chondrodite or staurolite, it is necessary to use a high temperature in the original heating. If constituents like SO_3, S, Cl or F are present it is necessary to add as retainer a substance such as lime, previously ignited and cooled. Add about 0.2 g through the thistle tube after the rock powder has been weighed.

To correct for the loss of water by evaporation, assume that 0.0003 g of water is lost per hour. If considerable carbon dioxide is present as carbonate in the powder, assume that each gram of CO_2 escaping from the tube will cause the loss of 0.0096 g of water.

Method of Gooch

The tubulated crucible devised by Gooch is useful for the determination of hydrogen (or water) in minerals which require a flux and a high temperature. Mix 0.5 g of the powder with 2.5 g of fully dehydrated sodium carbonate (heated nearly to melting and cooled in a desiccator) in the crucible *C*, Fig. 100. Place the crucible on a triangle, put the top in place and connect on one side with a calcium chloride tower and soda-lime tubes to free the air from moisture and carbon dioxide and connect on the other side with a sulfuric acid bulb-tube. If it is desired to determine carbon at the same time, use 10 g of fused lead chromate instead of the sodium carbonate as flux. Seal the top of the crucible by pouring powdered sodium tungstate (free from arsenic which would ruin the crucible), or sodium carbonate, into the flanged lip *L*, immerse the crucible in cold water and melt the flux in the lip by the flame from a blast lamp. As soon as the flux is fused withdraw the flame and stopper the tubes through which air is passed. When the flux cools, a tight joint is made as shown by the maintenance of the height of sulfuric acid in the bulb-tube as it is suck back during the contraction of the crucible on cooling.

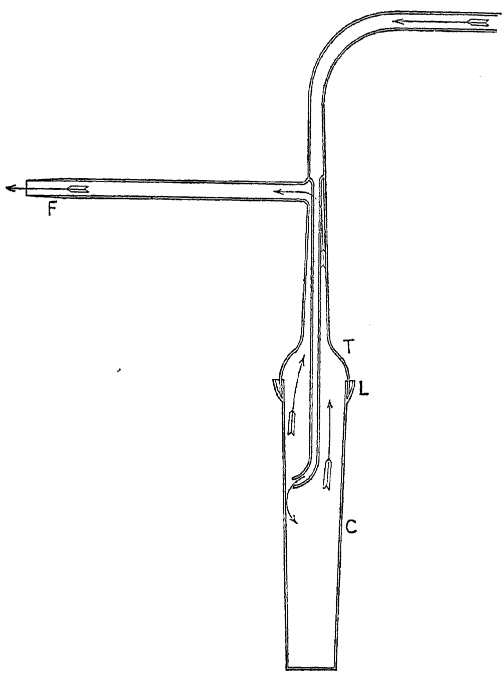


Fig. 100.

Dry at 105° for an hour by means of an air or toluene bath wh passing dry air through the crucible. Then connect the crucible witl weighed calcium chloride tube and the tube with a weighed ascar bulb (p. 362) if the determination of carbon is to be made also. Shi

the sodium tungstate joint from the flame by a horizontal piece of asbestos board and place a similar vertical shield between the crucible and the weighed absorption tubes. Connect the outer absorption tube with the sulfuric acid bulb to show the rate at which the gas is passing through the apparatus. Slacken the air stream and carefully heat the crucible with a free flame, beginning at the top of the rock mixture. When the fusion is complete, as shown by a lessening of the rate at which gas escapes, extinguish the flame and allow a current of air to continue until the apparatus is cold. Only a few minutes are required for the heating. Cool and weigh the absorption bulb with the usual precautions.

Obviously the determination can be made in a glass tube in a short combustion furnace.

Analysis of Tantalite (Columbite)*

Tantalite and columbite are isomorphous orthorhombic minerals containing tantalic and columbic acids in combination with ferrous and manganous oxides: $(Ta, Cb)_2O_5 \cdot (Fe, Mn)O$. Tantalic acid preponderates in tantalite; columbic acid, in columbite. The method given below permits the determination of the essential constituents of the mineral in a sample weighing 0.25 g or less.

Grind the mineral to an impalpable powder, and fuse 0.5 g with 4 g of potassium bisulfate in a silica crucible. Spread the fluid melt so that it solidifies in a thin layer. Cool, and fill the crucible with part of the hot solvent (4 g of tartaric acid in 50 ml of water). When detached, transfer everything to a 400-ml beaker with hot water, rinse the crucible, and add the rest of the solvent. Stir the liquid without interruption until the cake has disintegrated, leaving a pulverulent white residue which dissolves to a clear solution when the liquid is subsequently heated just to boiling during constant agitation. If this residue is allowed to settle, it begins to cake and adhere to the beaker, part of the tantalic acid becoming insoluble; in such a case, filter off and retreat the insoluble fraction, or begin again with a fresh 0.5-g portion.

Treat the liquid with 5 ml of 10 per cent H_2SO_4, and introduce H_2S until it is cold. Stir in a little filter pulp, allow to stand for an hour or two, and collect the precipitate and residue. Wash with acidulated H_2S water; gently ignite in a porcelain crucible, and weigh as SnO_2 *plus* silicious gangue. Determine the tin as on p. 224.

The filtrate contains hydrogen sulfide, and the iron as ferrous salt. Heat it to boiling, add 30 to 35 ml of strong hydrochloric acid, and boil for 2 minutes (Vol. I, p. 566). Allow the white earth-acid precipitate

* Schoeller and Webb, *Analyst*, **59**, 669 (1934).

to settle, decant the clear liquid through an 11-cm filter, mix the precipitate with a liberal proportion of filter pulp, and transfer to the filter. With a stream of 0.2 N HCl from a wash-bottle, return the precipitate to the beaker, stir up well, again collect on the filter, and finish the washing. Ignite the wet precipitate in the tared silica crucible, and reserve (A).

Evaporate the filtrate from the earth-acid precipitate in a large beaker to small bulk, transfer to a 250-ml beaker, and evaporate to about 20 ml. Reduce the ferric salt with hydrogen sulfide, add a decided excess of strong ammonia and 10 ml of fresh ammonium sulfide solution. The precipitate contains all the iron, and all but a few milligrams of the manganese. Allow to stand for 2 hours, collect the precipitate on a 9-cm filter containing a small pad of filter pulp pressed into the apex, and wash with water containing ammonium sulfide and chloride. Ignite the precipitate, dissolve it in strong hydrochloric acid, and separate iron from manganese by the basic acetate process (p. 158).

Slightly acidify the filtrate from the sulfide precipitate with acetic acid, boil off hydrogen sulfide, and add a fresh solution of 1 g tannin and 5 g of ammonium acetate. The colored precipitate consists of the small earth-acid fraction not precipitated by hydrolysis with hydrochloric acid. Filter, wash the precipitate with 2 per cent ammonium chloride solution, and ignite in the silica crucible containing the major fraction (A). Leach the ignited precipitate in a small beaker with 0.5 N hydrochloric acid, make slightly ammoniacal, collect the precipitate, ignite strongly, and weigh as $Ta_2O_5 + Cb_2O_5$.* For the separation of tantalum from columbium, the precipitate is treated as indicated on p. 178 (tannin methods: No. 4).

The filtrate from the tannin precipitate contains a few milligrams of manganese. It is best to boil it down with a large excess of nitric acid and 5 ml of sulfuric acid for the destruction of the tannin, tartaric acid, and removal of chloride. Dilute the colorless final acid solution with water, and test the liquid colorimetrically with persulfate and silver nitrate (see p. 138).

* It is assumed that the mineral is substantially free from titania.

PART II

VOLUMETRIC ANALYSIS

A gravimetric analysis is accomplished by adding to the solution of the substance to be analyzed a reagent of only approximately known strength, separating one of the products of the reaction from the solution and weighing it. A *volumetric* analysis is made by causing the reaction to take place by means of a measured volume of a solution of accurately known strength (*titer*) and computing the amount of substance present by the volume of the solution which reacts with it (cf. p. 1). For this sort of analysis accurately calibrated measuring instruments are necessary.

Measuring Instruments

1. *Burets* are tubes of uniform bore throughout the entire length; they are graduated in milliliters* and are closed at the bottom, as shown in Fig. 101, by means of a glass stopcock, or with a piece of rubber tubing containing a glass bead *h*. The latter form was devised by Bunsen and is used as follows: Seize the tubing between the thumb and forefinger at the place where the glass bead is, and by means of a gentle pressure at the top of the bead, form a canal at one side of the bead through which the liquid will run out. Instead of the glass bead an ordinary pinchcock is sometimes used.

Besides the above forms of burets, a great many others are in use, but it is unnecessary to describe them here.

2. *Pipets.* — A distinction must be made between a *transfer* pipet and a *measuring* one. A transfer pipet has only one mark upon it, and serves for measuring off a definite amount of liquid. Transfer pipets are constructed in different forms; usually they consist of a glass tube with a cylindrical widening at the middle. The lower end is drawn out, leaving an opening about 0.5–1 mm wide. Pipets of this nature are constructed which will deliver respectively 1, 2, 5, 10, 20, 25, 50,

* The liter as defined by the U. S. Bureau of Standards represents a volume of 1000.027 cubic centimeters. The one-thousandth part of a liter is called the milliliter, abbreviated ml. It is almost but not quite the same as a cubic centimeter, or cc.

100, and 200 ml. For delivering these definite volumes of liquid, pipets are more accurate than burets or flasks.

Measuring pipets are buret-shaped tubes graduated in milliliters and drawn out at the lower end. They serve to measure out any desired amount of liquid and are obtained with a total capacity of 1, 2, 5, 10, 20, 25, and 50 ml.

3. *Measuring flasks* are flat-bottomed flasks with narrow necks provided with a mark, so that when they are filled to this point they will contain respectively 50, 100, 200, 250, 300, 500, 1000, and 2000 ml. They serve for the preparation of standard solutions and for the dilution of fluids to a definite volume.

4. *Measuring cylinders* are graduated in milliliters and are used only for rough measurements.

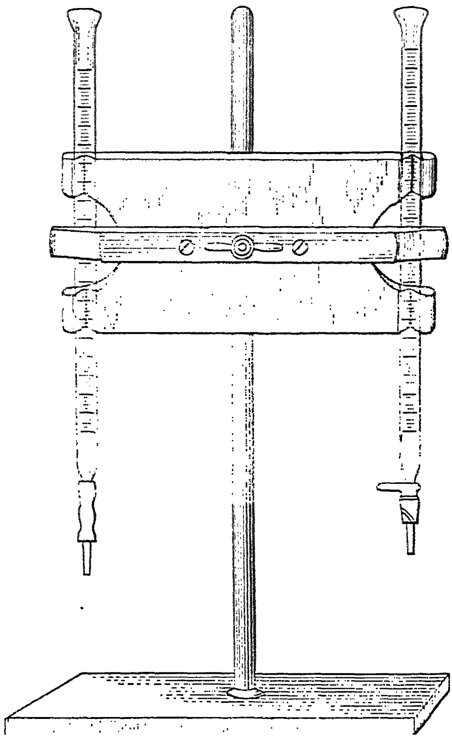


FIG. 101.

It is clear that accurate results can be obtained by a volumetric analysis only when the instruments used are accurately calibrated. It should never be taken for granted that a purchased instrument is correct, but it should always be tested carefully.

Normal Volume and Normal Temperature

A liter, which is the volume of a kilogram of water at its maximum density, is taken as the normal volume. If it is desired to mark on the neck of a liter flask the point to which this volume reaches, the position of the mark depends upon the temperature of the vessel. It is necessary, therefore, to choose for the vessel itself a definite temperature, the so-called *normal temperature.* At present the temperature of +20° C is taken as the normal temperature by the United States Bureau of Standards. According to this, then, the flask should contain

at 20° the volume that would be occupied by a kilogram of water at +4°, and as the kilogram is the unit of mass, the weighing should also take place in a vacuum.

DENSITY OF WATER AT DIFFERENT TEMPERATURES*

	Density		Density		Density
0°	0.999876	14°	0.999271	28	0.996258
1	9926	15	9126	29	0.995969
2	9968	16	8969	30	5672
3	9992	17	8801	31	5366
4	1.000000	18	8621	32	5052
5	0.999992	19	8430	33	0.994728
6	9968	20	8229	34	4397
7	9929	21	8017	35	4058
8	9876	22	0.997795	36	0.993711
9	9808	23	7563	37	3356
10	9727	24	7321	38	0.992993
11	9632	25	7069	39	2622
12	9524	26	0.996808	40	0.992244
13	9404	27	6538		

This experimental impossibility can be overcome inasmuch as the weight of a liter of water is known accurately at temperatures other than +4°, and also the expansion of the glass with rise of temperature, and the buoyancy which the weights and the water experience as a result of weighing in the atmosphere. The sum of the weights which must be placed upon the balance pan in order to determine the space occupied by a true liter of water, therefore, depends upon the temperature of the water and of the vessel, as well as the density of the air at the time of the experiment. The density of the air varies somewhat from day to day and depends upon the barometric pressure, the temperature, and the amount of moisture. It usually suffices, however, to assume the average values of these factors and in this way the table on p. 463 has been computed to show the apparent weight in air with brass weights for temperatures between 15° and 30° under 50 per cent humidity and a barometer reading of 760 mm.

If the glass vessel is at 20° no other correction is necessary. The glass, however, expands with rise of temperature. The coefficient of cubical expansion† varies from 0.000023 to 0.000028 per degree C. An average value of 0.000025 can be assumed.

* Thiesen, Scheel, and Diesselhorst, 1904. The values given represent the weight in grams of 1 ml of water with proper allowance made for the buoyancy of air; in other words, it gives the weight which would be obtained if it were possible to weigh the water in a perfect vacuum.

† At first sight it may seem strange to consider the *cubical* expansion of glass in calibrating. If, however, we consider a cube of glass with a cavity cut in it of

APPARENT WEIGHT IN GRAMS OF WATER IN AIR

Temp. in Degrees C	2000 ml	1000 ml	500 ml	400 ml	300 ml	250 ml	150 ml
15	1996.11	998.05	499.03	399.22	299.42	249.52	149.71
16	1995.80	997.90	498.95	399.16	299.37	249.48	149.68
17	1995.48	997.74	498.87	399.10	299.32	249.43	149.66
18	1995.13	997.56	498.78	399.03	299.27	249.39	149.63
19	1994.76	997.38	498.69	398.95	299.21	249.34	149.61
20	1994.36	997.18	498.59	398.87	299.15	249.30	149.58
21	1993.95	996.97	498.49	398.79	299.09	249.24	149.55
22	1993.51	996.76	498.38	398.70	299.03	249.19	149.51
23	1993.06	996.53	498.26	398.61	298.96	249.13	149.48
24	1992.58	996.29	498.15	398.52	298.89	249.07	149.44
25	1992.09	996.04	498.02	398.42	298.81	249.01	149.41
26	1991.57	995.79	497.89	398.31	298.74	248.95	149.37
27	1991.04	995.52	497.76	398.21	298.66	248.88	149.33
28	1990.49	995.24	497.62	398.10	298.57	248.81	149.29
29	1989.92	994.96	497.48	397.98	298.49	248.74	149.24
30	1989.33	994.66	497.33	397.87	298.40	248.67	149.20

In order to determine the exact volume of a vessel by weighing the water it contains, we must therefore make allowance for the expansion of the water (which makes a given volume lighter), for the buoyancy of air (which makes a given weight of water lighter than it really is if the weighings are made with brass), and for the expansion or contraction of glass if the temperature is other than 20°. Since the first two corrections are in the direction that makes a liter of water weigh less and the correction for the expansion or contraction of the glass is almost negligible, it is evident that the number expressing the weight of a definite volume of water in grams will always be smaller at laboratory temperatures than the volume expressed in milliliters. Moreover, the difference between these numbers at temperatures ranging from 15° to 30° will vary from 2.1 to 4.8 units or from 0.21 to 0.41 hundredths of 1 per cent of the total weight. In testing calibrated glass liter flasks, where the volume is substantially correct, the following table shows the number to add to the apparent weight in grams of the water in air (with brass weights) to give the correct volume in milliliters.

This table can be used also for testing other volumes such as that of a 500-ml flask, a 100-ml flask, or a 50-ml pipet, using the proportionate fraction of the above values. Thus in testing a buret by weighing 10-ml

10-cm edge, then on heating it the cavity will expand to the same extent as if the glass had not been cut out. We measure, therefore, the cubic expansion of glass which has been removed in order to find the change in volume of a glass measuring

portions, add the above values in centigrams to the weight in grams, and the sum will show the volume in milliliters.

VOLUME OF ONE LITER FROM THE APPARENT WEIGHT OF WATER

Temp.	Add	Temp.	Add	Temp.	Add	Temp.	Add
15°	2.07	19.0	2.65	23.0	3.40	27.0	4.31
15.5	2.13	19.5	2.73	23.5	3.50	27.5	4.43
16.0	2.20	20.0	2.82	24.0	3.61	28.0	4.56
16.5	2.27	20.5	2.91	24.5	3.72	28.5	4.69
17.0	2.34	21.0	3.00	25.0	3.83	29.0	4.82
17.5	2.41	21.5	3.10	25.5	3.95	29.5	4.95
18.0	2.49	22.0	3.19	26.0	4.06	30.0	5.08
18.5	2.57	22.5	3.29	26.5	4.18		

The above table is useful, but the student should know how to make the corrections without the table; the following example will show how this can be done.

Problem. — Compute the volume at the standard temperature of 20° of a glass measuring-flask from the following data:

Weight of flask filled to the mark with water at 24°	1136.40 g
Weight of the flask empty	140.58
Density of water at 24°	0.99732
Coefficient of cubical expansion of glass, per degree	0.000025
Density of weights, 8.4. Weight of 1 ml of air at 24° and 760 mm	0.00116 g

Reduction to Vacuum. — Since the flask is weighed twice under the same conditions, it is unnecessary to correct its weight for the buoyancy due to air, but the observed weight of water, 1136.40 − 140.58 = 995.82 g, needs correction. In making the buoyancy correction only two significant figures are reliable here because the density of the weights was not given with greater accuracy. The volume of air displaced by the water is very nearly 1000 ml and that of the air displaced by the weights is 1000/8.4 = 120 ml. The buoyancy correction is, therefore, the weight of 880 ml of air; 880 × 0.00116 = 1.02 g. The water in the flask would weigh 995.82 + 1.02 = 996.84 g, if the weight could be made in a perfect vacuum.

Correction for Glass Expansion. — The capacity of the flask increases from 20° to 24° to the same extent that glass would expand if it were present in the space occupied by the water, namely 1000 × 0.000025 × 4 = 0.10 ml. Therefore, the volume will be 0.10 ml less at 20° than it is at 24°, and the weight of the water would be 996.84 − 0.10 = 996.74 g.

Computation of the True Volume. — Since the density of water at 24° is given as 0.99732 g, 1 l should weigh 997.32 g and a volume of 996.74 g corresponds to

This checks well with the value to be obtained by using the above table according to which 3.61 g should be added to the apparent weight in air; 995.82 + 3.61 = 999.43.

Calibration of a Buret

A buret will not drain properly unless it is clean on the inside so that visible drops of liquid do not adhere to the sides when the liquid is withdrawn. "Cleaning solution," made from potassium dichromate and concentrated sulfuric acid, is efficient for cleaning burets and other glass apparatus. Dissolve 2 g. of potassium dichromate in 5 ml of water, heating till the salt has all dissolved, cool the solution and add slowly, while stirring, about 65 ml of concentrated sulfuric acid. Considerable heat is evolved on adding the acid to the water. Fill the buret with the hot chromic acid solution and allow it to stand 15 minutes or longer. Since this cleaning solution attacks rubber, it is best to remove the rubber tubing from the end of a Mohr or plain buret and force the end into a medium-sized cork stopper. Place a beaker under the buret while it is standing with the cleaning solution in it.

After 15 minutes, let the solution run out and rinse out the buret at least four times with water. Then test to see that water drains freely without leaving drops adhering to the sides; if so, the cleaning process must be repeated. The cleaning solution can be kept and used repeatedly. It should be warm but not boiling hot when being used. Before pouring the used cleaning solution down the sink, remember to start water running freely so that the acid will be largely diluted and will not attack the piping.

Remove the stopcock of the glass-stoppered or Geissler buret, wipe it dry and also wipe the inside of the ground joint in the buret. Smear the surface with stopcock lubricant,* and replace in the buret. Fasten the stopcock in place with some No. 24 copper wire.

Fill the buret with distilled water and make sure that the water extends to the very tip of the stopper with no air bubble there. To remove the air from a plain buret, raise the tip so that it is above the bottom of the glass tube and allow water to run out from the upturned tip; the lighter air tends to flow upward. The buret is now ready to be calibrated. Drain out water so that the upper level is close to the zero-mark.

Weigh a 50-ml, flat-bottomed, narrow-necked flask to the nearest centigram. The outside of the flask must be dry but it is not necessary to have the inside dry or cleaned with chromic acid solution. It is a waste of time to read the weight closer than to the nearest centigram,

* Vaseline can be used as lubricant but is a little thin. *Lubriseal*, sold by the A. H. Thomas Co. of Philadelphia, is better. A good lubricant can be made by melting together on the water-bath, 16 parts of vaseline, 8 parts of pure gum rubber, and 1 part of paraffin.

because one cannot read the buret closer than to the nearest 0.01 ml, and rapid weighing is advantageous to avoid error due to evaporation. Record the weight in the notebook. (See p. 467.)

Read the buret to the nearest 0.01 ml, and record the reading. Check each weight and each reading after setting them down in the notebook. In reading the buret, it is best to read the bottom of the meniscus, except with dark-colored liquids like potassium permanganate solution, in which case the top of the meniscus should be read. It is important that the eye should be directly opposite to the point read. If the eye is above the meniscus, the reading will be too high, and if the eye is too low the reading will be low. To avoid such parallax errors, the Bureau of Standards has asked the makers of burets to make the lines complete circles; the position of the eye is correct when the circle nearest to the bottom of the meniscus appears to be a straight line. When all the lines are circles, it is a little confusing to some eyes, so that some chemists prefer to use burets in which the lines of graduation do not extend very far and with lines of different lengths so that one can readily distinguish the whole and half milliliter lines. In such cases, it is well to take a strip of blue glazed paper with a straight and smooth edge. Wrap this strip around the buret evenly, with the colored edge on the inside. If the paper is placed about 2 divisions below the bottom of the meniscus, the eye will be level when the inside blue of the paper just comes into view. The blue also serves to make the tip of the meniscus appear a little darker and more sharply defined. With a little practice, one can easily learn to estimate to within 0.01 ml the exact position of the meniscus.

After reading the buret, drain out 10 ml of water into the weighed flask stopping as closely as possible to the 10.00 mark but not wasting much time trying to get it exactly there because there will be a slight drainage while the weighing is being made.

Then, without stopping to make an exact reading of the buret, weigh the flask and its contents to the nearest centigram. After this read the buret and allow water to run into the flask until the 20.00 mark is reached, continuing in this way until the buret has been drained to the lowest calibration mark. Record the weighings in the notebook according to the plan on the following page.

When the calibration is finished, fill the buret again and repeat the work. In the second testing the corrections for each 10 ml should check with the first within 0.02 ml. From the average values, make a plot using one division of vertical distance on the paper to represent 1 ml of buret reading and each division of horizontal distance to represent 0.01 ml of correction. Then, on the plot, the total distance from the

base line will show the correction to be applied for any given reading of the buret. Many burets are obtained today which are calibrated so accurately that there is no need of applying buret corrections, particularly if one always makes a practice to begin at about the zero-mark with every standardization and in every analysis. It is never safe, however, to assume that a buret is correct without testing it.

Instead of calibrating the buret in the manner just described, many chemists prefer to start each time at the zero-point, refilling the buret after each withdrawal of 10, 20, 30 or 40 ml of liquid. Others prefer to calibrate by causing the water to flow through a carefully calibrated small pipet, reading the buret after each withdrawal of a pipetful of water. The data obtained in calibrating a buret should be recorded as follows:

BURET CALIBRATION. TEMP. 25°

Wts.	Diff.	Buret Rdgs.	Diff.	True Vol.* of each portion	Correction for 10 ml	Total Correction
20.52		0.01				
30.50	9.98	9.96	9.95	10.02	+.07	+.07
40.52	10.02	19.95	9.99	10.06	+.07	+.14
50.47	9.95	29.93	9.98	9.99	+.01	+.15
60.39	9.92	39.91	9.98	9.96	−.02	+.13
70.40	10.01	49.85	9.94	10.05	+.11	+.24

* The table on p. 464 shows that the correction to be added to the weight of 1 l of water when weighed in the air at 25° is 3.83 g. For 10 ml (1/100 liter) the correction will be 0.0383 g. Since the buret cannot be read to less than 0.01 ml, the correction used is 0.04 g. For very accurate work, weight burets are used in which the stoppered buret is weighed at the start and finish of each analysis. With such a buret the analysis can be made more accurately; see p. 472.

Calibration of a Pipet

Clean the pipet with cleaning solution, but take care not to suck any of the chromic acid into the mouth. To avoid this, attach a piece of rubber tubing to the pipet and apply suction through this tubing. Rinse out the pipet with water. Suck up distilled water to a point above the graduation mark, quickly place the forefinger over the top of the tube and allow the level of the water to fall until the bottom of the meniscus coincides with the graduation mark. Then allow the contents of the pipet to run into a weighed flask; hold the pipet in a vertical position all the time. As soon as the pipet is empty, touch the tip to the inside surface of the flask and withdraw it. Do not wait for another drop to form and do not blow into the pipet. From the weight of the water, determine the volume of the pipet as in the calibration of a buret.

Calibration of a Flask

Flasks are sometimes calibrated both for content and for delivery. To test the calibration for delivery, clean and weigh the delivered water exactly the same as in the case of burets and pipets.

To test the calibration for content. Clean carefully and dry both inside and outside. Allow it to come to room temperature and weigh the empty flask. Then fill with water up to the mark and weigh again.

To calibrate an unmarked flask, preferably one having a narrow neck, clean, dry and weigh (or tare* carefully). Then place the proper weight on the balance pan and add water until equilibrium is again restored. Note the place on the neck where the bottom of the meniscus comes.

Place the flask upon a level surface and fasten a piece of gummed paper with a straight edge around the neck of the flask so that its upper edge is just tangent to the deepest point of the water meniscus. Empty the flask, dry, cover its neck with a uniform layer of beeswax, and allow to cool; this usually requires about 15 minutes. Then hold the flask, as is shown in Fig. 102, against the piece of wood *s*, place the blade of a pocket-knife firmly against the upper edge of the thick paper ring, and revolve the flask through 360° around its horizontal axis; in this way a circle is cut in the wax layer. By means of a feather place a drop of hydrofluoric acid† along this circle while holding the flask in the horizontal position. By turning the flask around its axis, allow the drop of hydrofluoric acid to act upon the glass where the wax coating has been cut. After 2 minutes wash the excess of hydrofluoric acid off, dry the neck of the flask by means of filter paper, heat until the wax melts, and wipe it off. Remove the last traces of wax by rubbing with a cloth wet with alcohol.

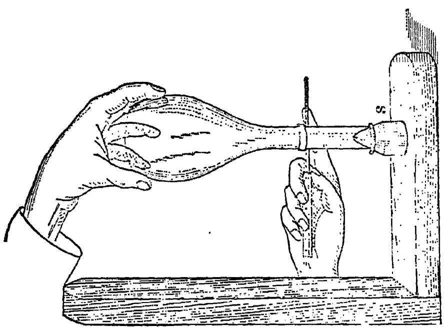


FIG. 102.

* The word *tare* is used to represent a counterpoise which may or may not be weights. If weights are used, it is not necessary to record the values.

† Hydrofluoric acid produces painful burns. If any of the acid gets on the fingers, wash them well with water *at once*. The acid does not smart, or sting, at first because it has anesthetic properties.

If flasks or burets are to be tested in large numbers, or when a class is set to work calibrating burets with a limited supply of balances, it is better to use a volumetric method. Thus for testing flasks at the Bureau

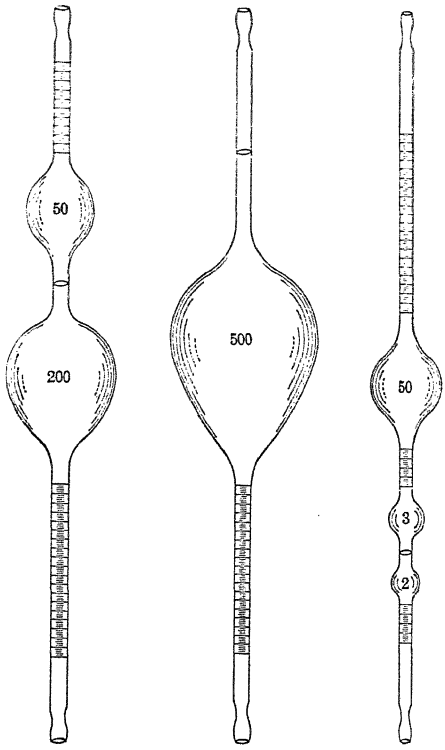


FIG. 103.

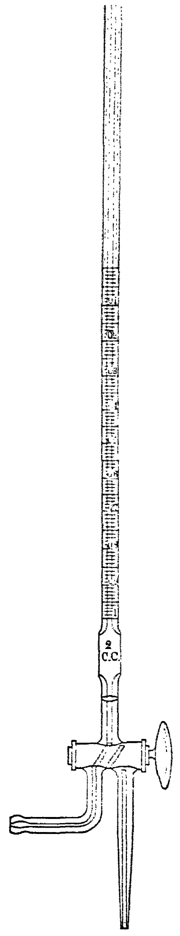


FIG. 104.

of Standards a series of volumetric standards have been made up, each standard having a capacity slightly less than that of the flask it is intended to test. When the water from the appropriate standard is delivered into a flask, the flask is filled nearly to the graduation mark. The filling is then completed by means of a finely graduated buret. The capacity of the flask is found from the known volume delivered by

the standard and the additional volume delivered by the buret. The flask standard and the buret are themselves calibrated by weighing the water delivered.

For the same purpose, Morse and Blalock devised a set of standard bulbs as shown in Figs. 103–106, inclusive. In calibrating these bulbs

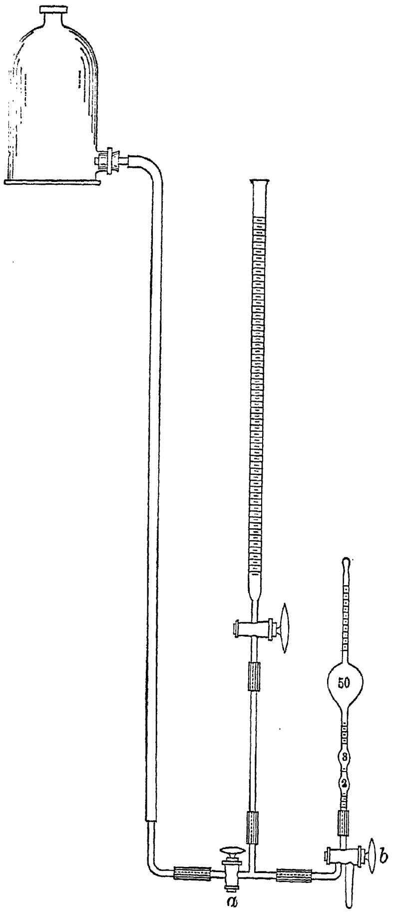


FIG. 105.

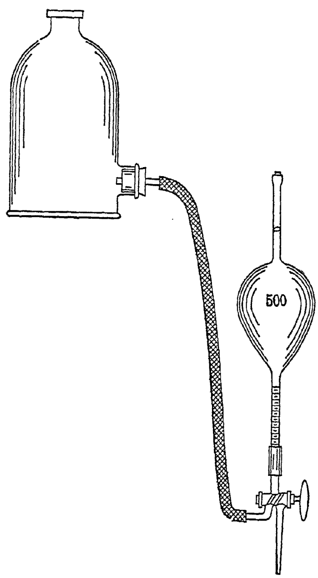


FIG. 106.

it is necessary to determine, with the aid of the table on p 4, the capacity from the single mark to the first stem division and th pacity of the stem for the smallest subdivision.

In using this Morse-Blalock apparatus it is not necessary to pay

any attention to the temperature after the calibration is once made because, if the temperature of the water is constant during the work, the volume of the flask or buret will correspond to that of the calibrating vessel.

To calibrate a standard bulb, first clean it with soapy water and chrome-sulfuric mixture as described on p. 465. Place the bulb so that the graduated stem is at the bottom as shown in Fig. 105. Use a glass stopcock for controlling the outflow, and the tip of the outflow must be restricted so that the outflow is not over 50 ml per minute. Fill the bulb to the upper mark. With the stopcock wide open allow water to flow into a weighed flask until the first division (zero) is reached. Stopper the flask and weigh. With the aid of the table on p. 464 compute the volume of water and capacity of the bulb. Adjust the liquid again to the zero-mark, place a smaller weighed flask under the delivery tube, and allow the stem to drain from the zero-mark down to the bottom mark. Weigh and compute the volume of each scale division with the aid of the data given in the tables. From these data compute the proper mark on the stem to which the water should fall in order to make the apparatus deliver the desired volume of water and check this by trial.

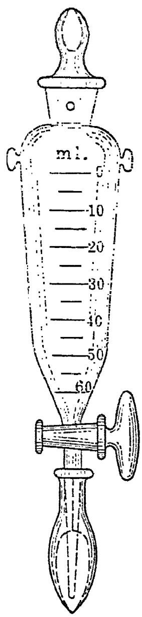


Fig. 107.

To calibrate a flask, place the flask under the delivery tube and allow water to run into it from the Morse-Blalock bulb until the proper mark on the stem is reached and mark the position of the water in the neck as described on p. 468.

To calibrate a buret, set up the apparatus as shown in Fig. 105. The reservoir must be higher than the top of the buret and this, in turn, must be placed so that the lowest graduation is higher than the bulbs. With the 3-way cock *b* closed, open the cock *a* and fill the buret with water. Close *a* and open *b* so that the 2-ml and 3-ml bulbs can fill, then drain the buret to the zero-mark and the bulbs to that mark on the stem of the 2-ml bulb which represents exactly 2 ml. This leaves the bulbs properly moistened. Leave the buret cock open. Turn the cock *b* and measure 5 ml of water from the buret into the small bulbs. Observe the position of the meniscus upon the stem of the 3-ml bulb and calculate the true capacity of the first portion of the buret from the values of the stem divisions as determined in the calibration of the bulbs.

For a more accurate calibration of the buret, 2-ml portions may be

withdrawn or, by means of the standard tube shown in Fig. 104, the value of each milliliter or any fraction may be determined.

For very accurate work, *weight* burets are desirable (Fig. 107). These are stoppered and weighed after each titration. It is possible to weigh a solution more accurately than to read its volume, but as a rule the end point is not accurate enough to warrant this extra bother of weighing.

Concentration of Solutions. Calculations of Volumetric Analysis

Volumetric analysis is based upon the measurement of volumes but it is necessary to know the strength of the reagent used to accomplish a given reaction. The strength of a solution is determined by its *concentration* or the quantity of reagent in a given volume. A solution of silver nitrate reagent may be prepared by dissolving 25 g of solid silver nitrate in water and diluting the solution to 1 l. The concentration of the well-mixed solution can be expressed by saying that it contains 25 g of silver nitrate per liter, or 25 mg per ml. This method of expressing concentrations in *weight per unit volume* is a very common one.

The chemist often speaks of a 10 per cent solution or a 20 per cent solution, etc. This is, as a rule, a rather careless way of expressing concentrations because the chemist usually means by a 10 per cent solution, as Wilhelm Ostwald pointed out, one that contains 10 g of reagent in 100 ml of solution. This method of expressing concentrations is used for approximate work when it does not make much difference whether the solution contains an exactly known weight.

In expressing the concentration of aqueous solutions of gaseous substances such as NH_3 or HCl it is common practice to say that the solution contains a certain *percentage by weight.* Thus the table at the back of the book shows that hydrochloric acid of 1.2 density contains 39.11 per cent HCl by weight. This means that 1 ml of the HCl solution weighs 1.2 g and contains 1.2×0.3911 g of dissolved HCl.

Sometimes mixtures of two liquids are said to contain a certain *percentage by volume* of one of them. Thus by diluting 25 ml of pure alcohol with water to make 100 ml of solution, the mixture can be said to contain 25 per cent of alcohol by volume.

The physical chemist usually finds it convenient to express concentrations in *moles per liter*, the designation *mole* (German *mol*) meaning a molecular weight in grams. A solution containing 36.46 g of HCl per liter is called, therefore, a *molal* solution. This designation is also applied to ions in solution; a solution is said to be molal in hydrogen ions if it contains 1.008 g of H^+ per liter.

Sometimes the molecular weight of a substance may be in doubt.

Thus one chemist may write the formula of mercurous chloride as HgCl and another chemist may prefer Hg_2Cl_2. A. A. Noyes, therefore, has made use of the term "formal solution" to represent one formula weight in grams per liter and gives the formula of the substance.

There are other ways in which concentrations can be expressed using other units of mass and of volume. Thus the mass can be expressed in grains, ounces, pounds or tons and the volume in pints, quarts, gallons, or cubic feet.

For the purposes of volumetric analysis none of the above methods of expressing concentration is entirely satisfactory. If we say that 1 ml of HCl solution contains 0.4693 g of dissolved HCl, it is a rather difficult problem in mental arithmetic to decide exactly how much NaOH or Na_2CO_3 it will neutralize. It involves the knowledge of the molecular weights of HCl, NaOH, and Na_2CO_3. We can carry out such a computation and find, for example, that 1 ml of the HCl solution will neutralize $0.4693 \times \frac{40.01}{36.46} = 0.5151$ g of NaOH. This value expresses the concentration of the acid solution in terms of NaOH and is useful if the acid is to be used for the sole purpose of analyzing samples of NaOH. Another computation is necessary to find out the strength of the solution with respect to any other substance with which it will react.

The most convenient method, however, of expressing the concentrations of solutions for the purposes of volumetric analysis is with reference to equivalent weights.

Normal Solutions

By a *normal solution* is understood one which contains 1 *gram-equivalent* of the active reagent dissolved in 1 l of solution.* By *gram-equivalent* is meant the amount of substance equivalent to 1 gram-atom (1.008 g) of hydrogen. One milliliter of a normal solution contains one *milli-equivalent* of active reagent. For convenience in computation the concentration of solutions used for volumetric purposes are expressed in terms of their normality; that is, a solution is 2 normal, 0.5 normal, 0.1 normal, etc. The letter N is used as an abbreviation for *normal.*

The gram-equivalent, or weight required to make a liter of normal solution, depends upon the nature of the reaction involved. It often happens that the same solution has a certain normal concentration when used for one purpose and a different normal concentration when

* It is important to note that a normal solution is not properly defined as one containing a gram-equivalent in 1 l of *solvent.* In volumetric analysis the unit is always referred to the volume of the solution.

used for another purpose. The reagents used in volumetric analysis are acids, bases, oxidizing agents, reducing agents, and precipitants.

The equivalent weight of an acid is determined by the number of replaceable hydrogen atoms in the acid molecule. Thus, to make a normal solution of the monobasic hydrochloric, hydrobromic, hydriodic, nitric, or acetic acids, it is necessary to have a molecular weight in grams (1 *mole*) of the acid dissolved in a liter of solution. To make 1 liter of normal solution of the dibasic sulfuric acid only $\frac{1}{2}$ mole of the acid is necessary.

Sometimes, however, it is not convenient to react with all the replaceable hydrogen atoms of an acid. In fact some acids are so weak that they cannot be used in volumetric analysis. Carbonic acid, for example, has no appreciable effect upon methyl orange and only 1 of the 2 hydrogen atoms in H_2CO_3 is acid toward phenolphthalein.

Phosphoric acid, H_3PO_4, really has 3 replaceable hydrogens, but only the first is acid toward methyl orange and 2 hydrogen atoms are acid toward phenolphthalein. In titrating with methyl orange, phosphoric acid acts as a monobasic acid and the normal solution contains 1 mole per liter. With phenolphthalein as an indicator, phosphoric acid acts as a dibasic acid and $\frac{1}{2}$ mole per liter will make a normal solution of phosphoric acid.

A normal solution of a base will contain 1 mole of replaceable hydroxyl. Thus of potassium hydroxide, KOH, sodium hydroxide, NaOH, and ammonium hydroxide, NH_4OH, 1 mole per liter makes a normal solution. Of barium hydroxide, $Ba(OH_2)$, calcium hydroxide, $Ca(OH)_2$, and strontium hydroxide, $Sr(OH)_2$, only $\frac{1}{2}$ mole per liter is required. Magnesium hydroxide is not appreciably soluble in water, but it is convenient to use the conception of normal solution to determine how much will be dissolved by an acid solution of known strength. One liter of normal hydrochloric acid will dissolve $\frac{1}{2}$ mole of $Mg(OH)_2$.

Salts of weak acids and strong bases have an alkaline reaction. With methyl orange as indicator, sodium carbonate, Na_2CO_3, reacts with 2 moles of hydrochloric acid; hence the equivalent weight is $\frac{1}{2}$ mole of sodium carbonate. With phenolphthalein, however, the end point is reached when 1 mole of sodium carbonate has reacted with 1 mole of hydrochloric acid; in this case the normal solution will contain 1 mole of sodium carbonate. Borax, $Na_2B_5O_7$, reacts with 2 molecules of hydrochloric acid when methyl orange is the indicator. If after this neutralization considerable glycerol, $C_3H_5(OH)_3$ or some mannitol, $C_6H_8(OH)_6$, is added another molecule of hydrochloric acid is required for each atom of boron in order to make the solution neutral to phenolphthalein.

The equivalent weight of an oxidizing agent is determined by the change in polarity which the reduced element experiences. The po-

larity of an element is the sum of the positive and negative valence bonds which it has in a compound; it represents the state of oxidation. Usually the polarity is the same as the valence except that a positive or negative sign is prefixed, but sometimes, as is true of the nitrogen atom of an ammonium salt, there is a difference. Nitrogen in the ammonium radical has a valence of 5, but four of the bonds are negative toward hydrogen atoms and the fifth bond is positive toward the acid ion of the ammonium salt. The polarity of nitrogen in an ammonium salt is -3 and it corresponds to the same state of oxidation as ammonia, NH_3.

When potassium permanganate is used as an oxidizing agent, the manganese drops to a lower polarity. In permanganate the polarity of the manganese atom is $+7$, and in most reactions used in volumetric analysis, the manganese is reduced to manganous salt in which the manganese has a polarity of $+2$:

$$MnO_4^- + 5\,Fe^{++} + 8\,H^+ \rightarrow Mn^{++} + 5\,Fe^{+++} + 4\,H_2O$$
$$2\,MnO_4^- + 10\,I^- + 16\,H^+ \rightarrow 2\,Mn^{++} + 5\,I_2 + 8\,H_2O$$

A normal solution of potassium permanganate, therefore, will contain $\frac{1}{5}$ mole of $KMnO_4$ because the atom of manganese loses 5 positive charges in changing from a polarity of $+7$ to $+2$.

Sometimes, however, the manganese of potassium permanganate is reduced only to the quadrivalent state. Thus a hot, nearly neutral solution of a manganous salt can be made to react with permanganate as follows:

$$2\,MnO_4^- + 3\,Mn^{++} + 2\,H_2O \rightarrow 5\,MnO_2 + \underline{4\,H^+}$$

In this case the manganese atom in permanganate only loses 3 charges and a normal solution of permanganate will contain only $\frac{1}{3}$ mole of the reagent. Usually permanganate is standardized by a reaction in which it is reduced to manganous salt. *Throughout this book, therefore, a normal solution of permanganate will refer to one containing* $\frac{1}{5}$ *mole of* $KMnO_4$ *per liter.*

Potassium dichromate is often used as an oxidizing agent. In it each chromium atom has a polarity of $+6$ and by reduction 2 trivalent chromic ions are formed. There is a loss in polarity of 3 charges for each chromium atom, and a normal solution of potassium dichromate, $K_2Cr_2O_7$, will contain $\frac{1}{6}$ mole.*

* The valence of an ion containing more than one element is the algebraic sum of the polarities of its constituents. Except in peroxides, oxygen has a polarity of -2 in its compounds. The polarity of the chromium can be determined from the charge of the ion and that of the oxygen. The same is true of the permanganate ion or of any other complex ion.

$$7\ H_2O$$
$$+\ 3\ I_2 + 7\ H_2O$$
$$Cr_2O_7^{=} + 3\ Sn^{++} + 14\ H^+ \rightarrow 2\ Cr^{+++} + 3\ Sn^{++++} + 7\ H_2O$$
$$Cr_2O_7^{=} + 3\ H_2S + 8\ H^+ \rightarrow 2\ Cr^{+++} + 3\ S + 7\ H_2O$$

A solution of a ferric salt is sometimes used as a mild oxidizing agent. Thus, it will oxidize the iodide anion

$$2\ Fe^{+++} + 2\ I^- = 2\ Fe^{++} + I_2$$

In this case, the oxidation depends upon the reduction of the ferric ion to the ferrous condition, and the equivalent weight of a ferric salt is the molecular weight divided by the number of Fe atoms in the molecule of the ferric salt.

Recently, solutions of ceric salts have been highly recommended for replacing potassium dichromate and potassium permanganate in titrations. The oxidizing effect of the quadrivalent cerium cation depends on the reduction of the cerium to the trivalent condition. The ceric cation, Ce^{++++}, is reduced to Ce^{+++} nearly as easily as MnO_4^- is reduced to Mn^{++}. Ceric solutions are more stable than permanganate solutions, but the end point in a titration is not so easy to find. Usually it is best to determine the end point potentiometrically or with the aid of a colored substance that changes color when oxidized, such as diphenylamine or diphenylamine sulfonic acid.

$$\cdot + Fe^{++} = Ce^{+++} + Fe^{+++}$$

The equivalent weight of a reducing agent is determined in like manner by the gain in polarity which the oxidized element experiences. Ferrous salts are oxidized to ferric salts and the iron is changed from +2 to +3 in polarity. A normal solution of ferrous sulfate, $FeSO_4 \cdot 7H_2O$, or of ferrous ammonium sulfate, $FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$, will contain 1 mole of either salt per liter.

As precipitants, the normal solutions are referred to the simplest type of salt in which each constituent has a valence of 1. Thus of sodium chloride, NaCl, and of silver nitrate, $AgNO_3$, a normal solution will contain 1 mole per liter. Of sodium sulfate, Na_2SO_4, barium chloride, $BaCl_2$, and magnesium sulfate, $MgSO_4$, a normal solution will contain $\frac{1}{2}$ mole per liter.

If potassium dichromate is used as a precipitant in the following reaction

$$Cr_2O_7^{=} + 2\ Ba^{++} + 2\ C_2H_3O_2^- + H_2O \rightarrow 2\ \mathbf{BaCrO_4} + 2\ HC_2H_3O_2$$

the normal solution will contain $\frac{1}{4}$ mole per liter.

Oxalic acid and the acid oxalates are used sometimes as acids and sometimes as reducing agents. Oxalic acid, $H_2C_2O_4$, has 2 replaceable hydrogens when titrated against alkali with phenolphthalein as indicator, and its normal solution as an acid contains $\frac{1}{2}$ mole per liter:

$$H_2C_2O_4 + 2\ NaOH \rightarrow Na_2C_2O_4 + 2\ H_2O$$

or
$$2\ H^+ + 2\ OH$$

Oxalic acid also reacts with permanganate in accordance with the following equation:

$$5\,C_2O_4^{=} + 2\,MnO_4^{-} + 16\,H^+ \rightarrow 2\,Mn^{++} + 8\,H_2O + 10\,CO_2$$

From the fact that the normal solution of permanganate contains $\frac{1}{5}$ mole per liter, it is clear that the equivalent weight of oxalic acid as a reducing agent is $\frac{1}{2}$ mole, just as when acting as an acid. In this case, however, the reducing power has nothing whatever to do with the hydrogen-ion content of oxalic acid, for the above reaction takes place in the presence of a mineral acid. The valence of carbon in oxalic acid is 4 and the structural symbol, leaving out the water of crystallization, is written thus:

$$\begin{array}{c} O = C - O - H \\ \quad | \qquad\qquad \\ O = C - O - H \end{array}$$

This structural symbol shows that 3 valence bonds of each carbon atom are positive toward 2 atoms of oxygen but, on the assumption that one end of each valence bond is positive and the other negative, 1 bond of a carbon atom is positive toward another atom of carbon. The polarity of 1 carbon atom is, therefore, +4, while that of the other carbon atom is +2. When oxalic acid is heated, H_2O, CO, and CO_2 are formed, which agrees with this assumption. The average polarity of the carbon in oxalic acid is +3.

The fact that the equivalent of $C_2O_4^{--}$ is $\frac{1}{2}$ mole is also shown by the fact that the oxidation can be expressed by the equation

$$C_2O_4^{--} - 2\,\epsilon = 2\,CO_2$$

the Greek letter ϵ being used to represent the charge of the electron.

Potassium acid oxalate, KHC_2O_4, can be used as an acid

$$KHC_2O_4 + KOH \rightarrow K_2C_2O_4 + H_2O$$

in which case the equivalent weight is 1 mole of KHC_2O_4, but as a reducing agent the reducing power is due to the oxalate group and a normal solution will contain only $\frac{1}{2}$ mole of KHC_2O_4. A solution of KHC_2O_4 which is normal as an acid will be $2\,N$ as a reducing agent.

Potassium tetroxalate behaves similarly. As an acid it has 3 replaceable hydrogens and the equivalent weight is $\frac{1}{3}$ mole:

$$KHC_2O_4 \cdot H_2C_2O_4 \cdot 2H_2O + 3\,NaOH \rightarrow KNaC_2O_4 + Na_2C_2O_4 + 5\,H_2O$$

As a reducing agent, potassium tetroxalate has two $C_2O_4^{=}$ groups and the equivalent weight is $\frac{1}{4}$ mole. If a solution of potassium tetroxalate

contains 1 mole per liter, it is $3N$ as an acid and $4N$ as a reducing agent, and the same relation holds at all concentrations.

Preparation of Normal Solutions

The required amount of substance should be dissolved in water and diluted to a volume of 1 l at 20°. Often, however, the water is not at the normal temperature, so that it is customary to dissolve the substance in water at the laboratory temperature and then dilute the solution up to the mark in a liter flask. After thoroughly mixing the solution, its temperature is taken by a sensitive thermometer. If the temperature is above 20°, the volume of the solution would be less than 1 l if it were cooled to exactly 20°, so that the solution as made up is a little too strong. The following table shows how to correct for the temperature effect:

TEMPERATURE CORRECTION FOR VOLUMETRIC SOLUTIONS

Temp. of measurement, °C	Capacity of apparatus in milliliters at 20° C						
	2000	1000	500	400	300	250	150
	Correction in milliliters to give volume of water at 20° C						
15	+1.54	+0.77	+0.38	+0.31	+0.23	+0.19	+0.12
16	+1.28	+0.64	+0.32	+0.26	+0.19	+0.16	+0.10
17	+0.99	+0.50	+0.25	+0.20	+0.15	+0.12	+0.07
18	+0.68	+0.34	+0.17	+0.14	+0.10	+0.08	+0.05
19	+0.35	+0.18	+0.09	+0.07	+0.05	+0.04	+0.03
21	−0.37	−0.18	−0.09	−0.07	−0.06	−0.05	−0.03
22	−0.77	−0.38	−0.19	−0.15	−0.12	−0.10	−0.06
23	−1.18	−0.59	−0.30	−0.24	−0.18	−0.15	−0.09
24	−1.61	−0.81	−0.40	−0.32	−0.24	−0.20	−0.12
25	−2.07	−1.03	−0.52	−0.41	−0.31	−0.26	−0.15
26	−2.54	−1.27	−0.64	−0.51	−0.38	−0.32	−0.19
27	−3.03	−1.52	−0.76	−0.51	−0.46	−0.38	−0.23
28	−3.55	−1.77	−0.89	−0.71	−0.53	−0.44	−0.27
29	−4.08	−2.04	−1.02	−0.82	−0.61	−0.51	−0.31
30	−4.62	−2.31	−1.16	−0.92	−0.69	−0.58	−0.35

[This table gives the correction to various observed volumes of water, measured at the designated temperatures, to give the volume at the standard temperature, 20° C. Conversely, by subtracting the corrections from the volume desired at 20° C, the volume that must be measured out at the designated temperature in order to give the desired volume at 20° C will be obtained. It is assumed that the volumes are measured in glass apparatus having a coefficient of cubical expansion of 0.000025 per degree centigrade. The table is applicable to dilute aqueous solutions having the same coefficient of expansion as water.]

For the following standard solutions more accurate results will be obtained if the numerical values of the above corrections are increased by the percentages given below:

Solution	Normality		
	N	$N/2$	$N/10$
HNO_3	50	25	6
H_2SO_4	45	25	5
$NaOH$	40	25	5
KOH	40	20	4
HCl	25	15	3
$H_2C_2O_4$	30	15	3
Na_2CO_3	40	25	5

Standardization of Solutions

If the reagent to be used in a volumetric analysis is known to be pure, it is best to prepare the standard solution as outlined on p. 472. Frequently, however, it is better to determine the concentration by testing the strength of the solution against some other substance known to be pure. Thus the strength of an acid solution can be determined by weighing out some carefully purified sodium carbonate and determining exactly how much of the acid solution is required to neutralize this weight of pure sodium carbonate. In this case the acid solution is said to be *standardized against* sodium carbonate and sodium carbonate is called the *standard* substance. Evidently if the acid is a *normal* solution, each milliliter of solution will neutralize exactly 1 milli-equivalent of the standard. The normal solution not only contains 1 milli-equivalent of the active reagent in 1 ml but it will react with 1 milli-equivalent of other substances. In any standardization, therefore, if g is the weight of standard taken, ml is the number of milliliters of solution required to react with this weight of standard, and e is the milli-equivalent weight of the standard used, then the *normality* of the solution (or the number of milli-equivalents in 1 ml) is $\frac{g}{ml \times e} = N$. Usually this is sufficient because the weight of substance that reacts with 1 ml of the standardized solution can be found by multiplying the milli-equivalent weight of the substance analyzed by the value N. Sometimes, however, it is better to make the solution exactly normal, half-normal, or tenth-normal. To do this it is best to prepare the solution a little stronger than desired and then dilute it with water until the desired concentration is obtained. Then if N is the normal concentration originally

obtained, N' is the desired normality, V is the original volume taken and V' is the volume after dilution, $N \times V = N' \times V'$ and $V' = \frac{N \times V}{N'}$. $V' - V$ is then the volume of water to be added to the volume V.

In volumetric work it is often desirable to have two solutions of reagents, one having the opposite effect to the other. Thus in working with an acid, sometimes too much is added and it is convenient to have a standardized solution of a base at hand to neutralize the excess acid. It is not necessary to standardize the second solution independently but it is important to know the relative strengths of the two solutions.

If a milliliters of solution A are equal in strength to b milliliters of solution B, then 1 ml of $A = \frac{b}{a}$ milliliters of B and 1 ml of $B = \frac{a}{b}$ milliliters of A. If solution A is N-normal, then solution B is $\frac{a \times N}{b}$ normal. If, on the other hand, the solution A is known to be N-normal and solution B is known to be M-normal, then the relative strengths are

$$1 \text{ ml of solution } A = \frac{N}{M} \text{ milliliters of solution } B$$

$$1 \text{ ml of solution } B = \frac{M}{N} \text{ milliliters of solution } A$$

General Method of Computing Results

Let ml represent the volume in milliliters of N-normal solution required to react with s grams of a substance of which the milli-equivalent weight is e,

then
$$\frac{ml \times N \times e \times 100}{s} = \text{per cent}$$

In the analysis of sodium carbonate, molecular weight 106.0, completely neutralized by hydrochloric acid, the value of e is 0.0530 and the result obtained by the above formula will be the percentage of Na_2CO_3 in the sample analyzed. If it is desired to express the result in terms of Na_2O, molecular weight 62.0, the value of e is 0.0310. Or it may be desired to find the percentage of CO_2 in the sample on the assumption that nothing else but Na_2CO_3 is present that will react with the acid used. In this case the value of e is 0.022. In using the above formula, therefore, it is necessary to bear in mind that the value of the milli-equivalent should be in terms of the substance desired.

Sometimes, it is desirable to avoid computations in technical work and it is convenient to weigh out a sample such that the buret reading will give the percentage desired. This will be always the case if the weight of sample is $100 \times N \times e$, as inspection of the above equation will show. Or, if the weight of sample is $50 \times N \times e$, then the desired percentage will be found by multiplying the *ml* used by 2.

Subdivisions of Volumetric Analysis

I. Acidimetry and Alkalimetry.
II. Oxidation and Reduction Processes.
III. Precipitation Processes.

I. ACIDIMETRY AND ALKALIMETRY

This covers the analysis of acids and bases. In order to determine the amount of acid present, an alkaline solution of known strength is required; and conversely, in the analysis of a base, an acid solution is required. In both cases the " end point " of the reaction is determined with the help of a suitable indicator. The accuracy of the result depends largely upon the choice of the indicator, so that at this place a few words will be said with regard to the indicators most frequently used for detecting the presence of acids or alkalies.

The useful reactions of analytical chemistry are those which take place practically completely in a given direction. Such reactions are those in which a slightly ionized substance is formed, an insoluble precipitate is obtained, a gas is evolved, or there is an oxidation of one substance at the expense of another. The law of chemical mass action applied to a reaction of the type $A + B \rightarrow C + D$ tells us that a reaction may be expected to go to completion if one of the products, either C or D, is removed as fast as it is formed and this is the case when the substance is not ionized, is insoluble, or is a gas. The reason that the reaction $NaOH + HCl = NaCl + H_2O$ takes place in dilute solutions is that water is ionized but slightly and, from the standpoint of the electrolytic dissociation theory, the reaction of neutralization is really

$$H^+ + OH^- = H_2O$$

This is shown by the fact that the heat evolved by the reaction in dilute solution is practically the same irrespective of the nature of the ions that were originally combined with the H^+ and OH^- provided the original acid and base are both ionized almost completely.

The mass-action law, applied to the ionization of water, tells us that a

state of equilibrium exists when

$$= \text{a constant}$$

In these mass-action expressions, a symbol written inside a bracket signifies a concentration expressed in moles per liter. In the case of water, the concentration of the non-ionized H_2O is not changed appreciably as a result of ionization at room temperatures, and its concentration is enormous compared to the concentration of its ions; the above expression can be simplified, therefore, by saying $[H^+] \times [OH^-] = K_w = 1.2 \times 10^{-14}$ at 25°. This expression is of fundamental importance. It states that in any aqueous solution the concentration of hydrogen ions (expressed in moles per liter) multiplied by the concentration of the hydroxyl ions present (also expressed in moles per liter) always equals 1.2×10^{-14} at 25°.* Since 1 mole of H^+ and 1 mole of OH^- are formed from each mole of ionized water, it is evident that, in absolutely neutral water, the concentration of each of these ions is 1.1×10^{-7}.

Very small numbers, such as 0.000 000 12, are conveniently written as a number between 0 and 10 multiplied by 10 raised to the appropriate negative power. An accurate method for determining the hydrogen-ion concentration of a solution is to measure the electromotive force of a so-called "hydrogen electrode"† when immersed in the solution. If the electromotive force of this electrode in a normal solution of H^+ is taken as an arbitrary zero, then the concentration of a given solution can be found by the expression $E_{18°} = 0.058 \log \frac{1}{[H^+]}$ in which $E_{18°}$ represents the electromotive force, or electrode-potential, of the hydrogen electrode at 18°. The observed potential of the hydrogen electrode therefore is directly proportional to $\log \frac{1}{[H^+]}$. Sörensen proposed that this value be called the *hydrogen exponent* with the designation p_H. This proposal met with general approval and is used not only in science but also in chemical industries, because many chemical processes are sensitive to changes in acidity or alkalinity and it is easier to state that a certain reaction takes place to the best advantage at, say, $p_H = 12$

* The ionization constant of water, K_w, varies from 0.12×10^{-14} at 0° to 73×10^{-14} at 100° C.

† The hydrogen electrode is obtained by coating a platinum or gold wire with platinum black and dipping it into a solution which is kept saturated with pure hydrogen gas. The gas usually enters the solution through a tube containing the electrode.

than to say that the solution should have a hydrogen-ion concentration of 10^{-12} mole per liter.

Since in any solution $[H^+] \times [OH^-] = 1.2 \times 10^{-14}$, it is clear that the concentration of the OH^- is known as soon as the concentration of the H^+ is stated. The same is true of the p_H and p_{OH} values; the latter signifies the log $\frac{1}{[OH^-]}$ when $[OH^-]$ represents the concentration of hydroxyl ions in moles per liter. In all cases $p_H + p_{OH} = 14$ at 25°.

A perfectly neutral solution has a p_H value of 7. If the p_H value is smaller than 7, the solution can be said to be more acid than pure water, and if it is larger than 7 it is more basic. Another way of expressing this is to say that a solution is acidic if it contains more hydrogen ions per unit volume than are present in pure water and basic if it contains less hydrogen ions. It is well known that acids and bases vary greatly with respect to their ionization in aqueous solutions. The relative strengths is shown by a comparison of the ionization constants.*

When a strong acid, like hydrochloric acid, is neutralized with a strong base, such as sodium hydroxide, the reaction takes place practically completely as soon as exactly one equivalent of the base has been added. There is no appreciable hydrolysis of the salt formed, and the end point takes place at $p_H = 7$. It is a different matter when a weak acid like acetic acid is neutralized with sodium hydroxide. In this case the sodium acetate as it is formed tends to repress the ionization of the unneutralized acid, and when, finally, a quantity of base equivalent to

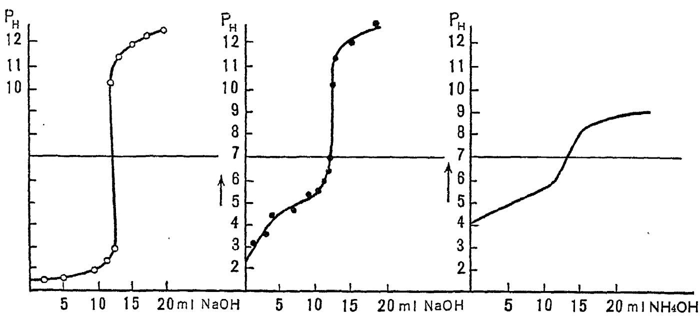
* The mass-action law applied to the ionization of a weak acid takes the general form $\frac{[H^+] \times [A^-]}{[HA]} = k$ in which k is called the *ionization constant.* Dibasic and tribasic acids are usually ionized to different degrees with respect to each replaceable hydrogen atom. The primary ionization constant of H_3PO_4 is $\frac{[H^+] \times [H_2PO_4^-]}{[H_3PO_4]} = 1.1 \times 10^{-2}$, the secondary ionization constant is $= 2.0 \times 10^{-7}$, and the tertiary ionization constant is $\frac{[H^+]\,[PO_4^{---}]}{[HPO_4^{--}]} = 3.6 \times 10^{-13}$.

The value 3.6×10^{-13} for the tertiary ionization of phosphoric acid shows that the presence of a considerable quantity of HPO_4^- in an aqueous solution does not increase very much the concentration of the hydrogen ions present over the quantity furnished as a result of the ionization of water itself.

The mass-action law applied to the ionization of a *strong acid* or of a *strong base* does not give a useful value because if the ionization is practically complete, the value of the ionization constant approaches ∞. In comparing the ionization constants, therefore, it is customary to call that of the strong acids and bases [1] and the number is enclosed in brackets to show that it is not obtained by a rigid application of the mass-action law.

the original acetic acid has been added, the p_H of the solution will be distinctly higher than 7. In the same way, when sodium acetate is dissolved in water, the solution will show $p_H > 7$. If a weak base like NH_4OH is neutralized with a strong acid like hydrochloric acid, the final solution will show a p_H distinctly less than 7.

The following curves obtained by measurement of the single potential of a hydrogen electrode during a titration will illustrate these points. The curve for the titration of the hydrochloric acid with sodium hydroxide shows a marked change produced by a very little base when the end point is reached. This may be taken as the half-way point of the nearly vertical line and corresponds almost exactly to $p_H = 7$. The curve for the titration of the acetic acid shows a distinct rise in p_H long before the end point is reached, and the half-way point of the nearly vertical line is at a $p_H > 7$. The third curve shows an indistinct end point, although the solution is neutral with $p_H = 7$ when an equivalent of base has been added. The indistinct end point is due to the fact that the ionization of both acid and the base is slight in the presence of their neutral salt; as a result, ammonium acetate is hydrolyzed appreciably in aqueous solution.



Titration of 0.1 N HCl with 0.1 N NaOH — Titration of 0.1 N $HC_2H_3O_2$ with 0.1 N NaOH — Titration of 0.1 N $HC_2H_3O_2$ with 0.1 N NH_4OH

From what has just been said four conclusions can be drawn: (1) the end point of a titration of an acid with a base does not always coincide with $p_H = 7$; (2) a good end point cannot be obtained if both the acid and the base are weak; (3) when a weak acid is titrated with a strong base, the end point occurs at $p_H > 7$; and (4) when a weak base is titrated with a strong acid the end point occurs at $p_H < 7$.

Indicators

The indicators used in acidimetry and alkalimetry are dyestuffs which are of one color in acid solutions and another color in basic solutions. They are, as a rule, weak acids; though some of them are weak

bases. It has been found that in organic compounds the color can usually be traced to a particular arrangement of atoms called a *chromophor*. The change in color, therefore, is caused by a slight rearrangement of the atoms in the molecule. Thus, if the salt of an indicator acid is yellow and on treatment with acid it turns red, this is due to the fact that, when the indicator acid is liberated by the action of the stronger acid, the molecule undergoes a slight change in the way the atoms are linked together and thereby loses temporarily the ability to ionize as an acid. It is not sufficient, however, to assume that this change of color is caused solely by the fact that the ions have a color other than that of the undissociated molecule; on the contrary, it has been shown in certain cases that the ions have the same color that the undissociated molecule has before the rearrangement of the atoms in the molecule has taken place. On the other hand, as regards the proper use of indicators it is necessary simply to bear in mind how salts of weak acids behave in the presence of stronger acids and how the acids themselves behave in the presence of alkali.

By means of electrometric tests it is possible to determine the hydrogen-ion concentration at which any indicator changes color. Indicators are known which change at different concentrations of hydrogen ion, and for any special case an indicator should be chosen which will change color as nearly as possible at the hydrogen-ion concentration corresponding to the saturation point of the acid and base used in the analysis.

As a result of comparisons between colorimetric and electrometric methods for the determination of hydrogen-ion concentrations in solutions of interest to biologists, Clark and Lubs* suggested the use of the following indicators:

Chemical Name	Common Name	Color Change	p_H Range
Thymolsulfonphthalein	Thymol blue	Red-yellow	1.2–2.8
Tetrabromophenolsulfonphthalein	Bromophenol blue	Yellow-blue	3.0–4.6
o-Carboxybenzeneazodimethylaniline	Methyl red	Red-yellow	4.4–6.0
Dibromo-*o*-cresolsulfonphthalein	Bromocresol purple	Yellow-purple	5.2–6.8
Dibromothymolsulfonphthalein	Bromothymol blue	Yellow-blue	6.0–7.6
Phenolsulfonphthalein	Phenol red	Yellow-red	6.8–8.4
o-Cresolsulfonphthalein	Cresol red	Yellow-red	7.2–8.8
Thymolsulfonphthalein	Thymol blue	Yellow-blue	8.0–9.6
o-Cresolphthalein	Cresolphthalein	Colorless-red	8.2–9.8

* *J. Bacteriol.*, **2**, 1, 109, 191 (1917); cf. *The Determination of Hydrogen Ions*, by W. M. Clark.

To prepare suitable indicator solutions, triturate 0.1 g of each of the above powders, excepting methyl red and *o*-cresolphthalein, with an equivalent quantity of 0.05 N solution of sodium hydroxide. Dilute with water to 500 ml in the case of cresol red and phenol red and to 250 ml in the case of thymol blue, bromothymol blue, bromophenol blue, and bromocresol purple. With methyl red, dissolve 0.5 g in 300 ml of alcohol and dilute with water to 500 ml. With *o*-cresolphthalein, dissolve 0.1 g in 500 ml of 95 per cent alcohol.

The indicators most used in quantitative analysis are *methyl orange*, *methyl red*, and *phenolphthalein*.

1. Methyl Orange

Under methyl orange,* Lunge,† who first proposed the use of this indicator, understood either the free sulfonic acid of dimethyl-amino-azo-benzene or its sodium or ammonium salt.

In the free state, the sulfonic acid is obtained in the form of reddish violet scales, soluble in considerable water. If some of the solid is dissolved in as little water as possible, a distinct reddish orange colored solution is obtained; but on the further addition of water this color gradually changes to yellow. If a trace of an acid is added to the yellow solution, it becomes red again, and on further dilution with water the color changes to orange and finally to yellow once more, if too much acid was not added. The color change which takes place between $p_H = 2.9$–4.0 can be easily explained.

In the sensitive neutral solution there is a condition of equilibrium between two isomeric forms of methyl orange as expressed by the equation:

$$HSO_3 \cdot C_6H_4 \cdot N{:}N \cdot C_6H_4N(CH_3)_2 \rightleftarrows SO_3 \cdot C_6H_4 \cdot NH \cdot N{:}C_6H_4{:}N(CH_3)_2$$

The formula on the left represents the yellow substance and the color is due to the azo group N : N, whereas the formula on the right represents the red substance which has for its chromophor the quinoid group $:C_6H_4:$. The formula on the left has a sulfonic group which imparts acid properties to the molecule and at the other end is an $N(CH_3)_2$ group which has weakly basic properties. The formula on the right, therefore, represents an inner salt inasmuch as the acid and base forming groups are united.

The sodium salt of methyl orange is yellow and has the formula

$$NaSO_3 \cdot C_6H_4N : NC_6H_4N(CH_3)_2$$

* This dyestuff is known commercially as helianthin, orange III, tropäolin D, Poirrier's orange III, dimethylaniline orange, mandarine orange, and gold orange.

† *Berichte*, **1878**, II, 1944; *Chem. Industrie*, **1881**, 348; *Handbuch für Sodaindustrie*, I, 52 (1879); II, 151 (1893).

and when decomposed by acids the free sulfonate at once reverts to the red form:*

$$SO_3 \cdot C_6H_4 \cdot NH \cdot N : C_6H_4 : N(CH_3)_2$$

Methyl orange is an excellent indicator for weak bases, but cannot be used for the titration of weak acids.

If it is desired to titrate a solution containing sodium hydroxide with a tenth-normal acid, add a little methyl orange to the alkaline solution and titrate with acid until the solution is colored a distinct red. The latter color will not appear permanently until an excess of the acid has been added. This causes a slight error in the analysis which is greater in proportion to the amount of indicator employed, and the more dilute the solution.

From what has been said the following rule holds:

In any titration a small amount of indicator should be used, and inasmuch as the change of color is proportional to the concentration and not to the absolute amount of acid present, the analyzed solution should have as nearly as possible the same concentration as was the case in the standardization of the solution added.

If a normal acid is used for the titration, the change of color is very sharp when the volume of the solution titrated amounts to about 100 ml. Even with a fifth-normal solution the change of color is very distinct, but less so with tenth-normal solutions; but these can be titrated provided the standardization was made at the same dilution as that used in the analysis.

How is it with the end point in the titration of an acid with an alkali hydroxide solution?

If a few drops of methyl orange are added to 100 ml of water, the water will be colored distinctly yellow. If the solution contains the same amount of hydrochloric acid as is contained in 10 ml of a tenth-normal solution of this acid, the solution will be colored a deep red. In order that the solution shall assume its original yellow color, it is only necessary to add exactly 10 ml of $0.1\,N$ alkali hydroxide solution, but no excess of alkali, because the water is itself sufficient to decompose the dyestuff sufficiently to produce the yellow color.

It is evident, then, that it is not a matter of indifference in the analysis whether the titration is completed by the addition of acid or by the addition of alkali. In the former case, for the titration of T milliliters of $0.1\,N$ alkali solution, $T + t$ milliliters of $0.1\,N$ acid would be necessary.

Methyl orange is more sensitive toward alkali than it is toward acid,

* Cf. Stieglitz, *J. Am. Chem. Soc.*, **25**, 1117.

but many prefer to finish the titration by the addition of acid, for most eyes can detect the change from yellow to red with greater accuracy. In principle it is more accurate to accomplish the titration the other way, as was recommended by F. Glaser.

Preparation of Methyl-orange Solution. — Dissolve 0.10 g of solid methyl orange* in 100 ml of hot water, allow to cool, and filter off any deposited meta-sulfonic acid. Use 1 drop for each 100 ml of solution.

Use. — Methyl orange is suitable for the titration of strong acids (HCl, HNO_3, H_2SO_4) as well as phosphoric and sulfurous acids. Hydrochloric and nitric acids can be titrated with this indicator with a sharper end point than sulfuric acid. If free phosphoric acid is titrated with sodium hydroxide using this indicator, the solution changes from red to yellow when one-third of the phosphoric acid has been neutralized:

$$H_3PO_4 + NaOH = NaH_2PO_4 + H_2O$$

The primary phosphates are neutral toward methyl orange; the secondary and tertiary phosphates react alkaline toward it. With half-normal solutions, the end point of the reaction is fairly sharp, with tenth-normal solutions it is less so; in the latter case an excess of about 0.3 ml of the tenth-normal alkali is necessary to cause the change from red to yellow.

Sulfurous Acid. — In titrating sulfurous acid with sodium hydroxide, the yellow color is obtained when half the acid has been neutralized

$$H_2SO_3 + NaOH = NaHSO_3 + H_2O$$

so that $NaHSO_3$ is neutral toward this indicator.

The weak acids HCN, H_2CO_3, H_2S, H_3AsO_3, H_3BO_3 and $HCrO_4^-$ when present in moderate quantities do not act upon the indicator. CO_2 and H_2S produce an orange-red coloration only when present in large amounts. For this reason dilute solutions of the alkali salts of these acids can be titrated with accuracy by means of this indicator.

Organic acids cannot be titrated with methyl orange.

The strong and weak bases $NaOH$, KOH, NH_4OH, $Ca(OH)_2$, $Sr(OH)_2$, $Ba(OH)_2$, and $Mg(OH)_2$ can be titrated with great accuracy by means of this indicator, and the same is true of the amine bases (methyl and ethyl amines, etc.); on the other hand, such weak bases as pyridine, aniline, and toluidine cannot be titrated.

Nitrous acid ordinarily cannot be titrated with this indicator because the acid destroys it. If, however, an excess of alkali is first added to

* Of the sodium salt dissolve 0.11 g in 100 ml of water, add 3.35 ml 0.1 *N* HCl, and after the solution has stood for some time filter off any deposited crystals.

the solution of nitrous acid, then the methyl orange, the titration can be accomplished with accuracy.

2. Methyl Red

$$(CH_3)_2\overset{4}{N} - C_6H_4 - \overset{1}{N} = \overset{2}{N} - C_6H_4 - \overset{1}{C}OOH$$

Para-dimethyl-aminoazo-benzene-o-carboxylic acid

This valuable indicator is suitable for titrating weak organic bases and ammonia. The aqueous solution of methyl red is orange, but if a few drops are added to 50–100 ml of water, the water is colored a pale yellow. The addition of a drop of 0.1 N HCl at once turns the liquid a violet-red without passing through any intermediate shade, and by the addition of a drop of ammonia the solution becomes nearly colorless again. Methyl red is not very sensitive toward carbonic acid, but more so than is methyl orange, so that it is less suitable for the titration of carbonates. The chief advantage of this indicator lies in the sharp color change from a very pale yellow to a violet-red, even in titrating ammonia. The color change is at $p_H = 4.4–6.0$.

Preparation of the Indicator. — Dissolve 0.10 g of the free acid in 60 ml of ethyl alcohol and dilute with 40 ml of water. Allow the solution to cool, and then filter. Add 2 drops of this solution to every 100 ml of the solution to be titrated.

3. Phenolphthalein

Phenolphthalein is a very weak acid forming red salts which contain the strongly chromophoric quinoid group: C_6H_4:. The free acid, however, is unstable and when set free from one of its colored salts reverts instantly into a colorless lactoid form, containing no chromophor group:

$$HOOC \cdot C_6H_4 \cdot C(C_6H_4OH) : C_6H_4 : O \rightleftarrows O \cdot OC \cdot C_6H_4 \cdot C(C_6H_4OH)_2$$

In the free acid, therefore, the condition of equilibrium favors the lactoid form and only minimal traces of the quinoid acid are present. This trace of quinoid acid is ionized and is in equilibrium with its ions:

$$HOOC \cdot C_6H_4 \cdot C(C_6H_4OH) : C_6H_4 : O$$
$$\rightleftarrows H^+ + OOC \cdot C_6H_4 \cdot C(C_6H_4OH) : C_6H_4 : O^-$$

The addition of an alkali causes the hydrogen ions to disappear, so that more of the quinoid molecules must be ionized to preserve equilibrium, and the quinoid molecules in turn are reproduced from the lactoid as fast as the former are converted into the salt. Phenolphthalein is

a very sensitive indicator towards acids, but on account of being a very weak acid it does not form stable salts with weak bases.

Preparation of the Indicator. — Dissolve 1 g of pure phenolphthalein in 100 ml of 90 per cent alcohol. Use 1 drop for each 100 ml of solution.

Uses. — Phenolphthalein is particularly suited for the titration of organic and inorganic acids and strong bases, but not for the titration of ammonia.

If the red-colored solution containing phenolphthalein and a little alkali is treated with an excess of concentrated alkali hydroxide solution, the red color disappears at p_H = 8.3–10 but returns on diluting the solution with water. Phenolphthalein, therefore, cannot be used as an indicator for the titration of concentrated alkali without previous dilution with water.

Phenolphthalein is a sensitive indicator toward acids, far more sensitive than methyl orange, for not only can the presence of weak acids be detected, but very small amounts can be titrated with accuracy.

Ordinary distilled water usually contains carbon dioxide, as can be shown by slowly adding 0.1 *N* barium hydroxide solution, drop by drop, to 100 ml of water containing a drop of the indicator solution. Where the alkali first meets the water, a red color is produced which disappears on stirring, so that often as much as 0.5 to 1.8 ml of the alkali must be added before a permanent red color is obtained. The disappearance of the red shows the presence of acid (in this case carbonic acid), and its amount corresponds to the alkali neutralized.

Phosphoric Acid. — If a solution of phosphoric acid containing phenolphthalein is titrated with normal sodium hydroxide solution, a permanent coloration is produced when two-thirds of the phosphoric acid is neutralized:

$$H_3PO_4 + 2\,OH^- \rightarrow HPO_4^{=} + 2\,H_2O$$

Apparently Na_2HPO_4 reacts neutral toward phenolphthalein, but this is not quite correct, for a pure solution of disodium phosphate is colored by phenolphthalein a pale pink, and on diluting with water the intensity of the color increases owing to progressive hydrolysis:

$$HPO_4^{=} + H_2O \rightleftarrows OH^- + H_2PO_4^-$$

During the titration of phosphoric acid with sodium hydroxide, a pale-pink color is obtained somewhat too soon, and this color gradually increases in intensity until finally a maximum is reached; this is taken as the end point. It is possible that this hydrolysis could be prevented by the addition of a large excess of sodium chloride and cooling to about 0° C.

Carbonic Acid. — If the solution of a neutral alkali carbonate is treated with phenolphthalein a red color is obtained, showing the presence of hydroxyl ions in the solution, due to hydrolysis:

$$CO_3^{=} + H_2O \rightleftarrows OH^- + HCO_3^-$$

If hydrochloric acid is added to such a solution which is not too dilute and is at a temperature of 0°, decolorization is effected when the alkali carbonate* is changed to bicarbonate. At ordinary temperatures a sharp end point cannot be obtained; the color gradually fades. Pure sodium bicarbonate dissolved in ice-cold water is not colored by the addition of phenolphthalein; if it is warmed to the temperature of the room it turns red, but on cooling the color disappears (Küster).

Silicic acid seems to be without influence upon phenolphthalein, for alkali silicates (the water-glasses) can be titrated with accuracy.

Chromic acid and acid chromates are changed by the addition of alkali to neutral chromates, which have no action upon phenolphthalein.

Alkali aluminates can be titrated accurately with this indicator, for aluminum hydroxide does not affect it.

4. Lacmoid, or Resorcin Blue,

Lacmoid is prepared by heating resorcinol with sodium nitrite at not too high a temperature. The constitution of the dye has not been completely established. Pure lacmoid is soluble in water (the impure product is difficultly soluble), but more soluble in alcohol, glacial acetic acid, acetone, and phenol, and less so in ether. To determine whether a sample of commercial lacmoid is suitable for use as an indicator, boil a little of it with water; if the water is colored an intense and beautiful blue, it can be used. In this case the alcoholic solution will be of a pure blue color, and not with a tinge of violet, as with the impure substance.

Preparation of Pure Lacmoid. — Filter the solution of the good commercial product in hot 96 per cent alcohol and allow it to evaporate in vacuo over concentrated sulfuric acid.

Preparation of the Indicator. — Use a solution containing 0.2 g of the purified lacmoid in 100 ml of alcohol.

Behavior of Lacmoid toward Acids and Bases. — If the solution after it has been colored reddish by acid is treated with a solution of an alkali hydroxide, the red color is gradually changed to a violet-red, and on fur-

* Alkaline-earth carbonates behave differently. They do not dissolve appreciably until the solution has a p_H smaller than 6. Cf. p. 513.

ther addition of alkali, it suddenly changes to a pure blue at $p_H = 5\text{–}6$. If the violet solution is diluted with considerable water, it becomes blue.

Uses. — Lacmoid is suitable for the titration of strong acids and bases as well as for ammonia, but is not suited for the titration of nitrous acid or weak acids.

5. Litmus

The chief coloring principle of litmus, the azolitmin, is a dark brown powder only slightly soluble in water and insoluble in alcohol and ether. With alkalies it forms a readily soluble blue salt. Besides the azolitmin, other dyestuffs are present in litmus which are soluble in alcohol with a red color.

Commercial litmus is obtained in small cubes mixed with considerable calcium carbonate; the dyestuffs are then in the form of their calcium salts, soluble in water. If the commercial material is dissolved in water, a solution of blue and reddish violet coloring matter is obtained, which becomes red on the addition of acid. On making alkaline again, a pure blue color is not obtained at first, but a reddish violet, which becomes blue on the addition of considerable alkali. Such a solution, therefore, is far from being a sensitive indicator and cannot be used for accurate work. A number of different methods have been proposed for obtaining a sensitive litmus solution, and that of F. Mohr* will be described.

Purification of Litmus. — Place the cubes of litmus in a porcelain dish (without powdering), cover with 85 per cent alcohol, and digest on the water-bath for some time with frequent stirring. Decant off the solution and repeat the operation 3 times. By this means the undesired coloring matter is removed. Extract the residue with hot water, and as it is very difficult to filter the solution, pour it into a tall cylinder, and after standing several days, siphon off the clear liquid. Evaporate the solution to about one-third of its volume and make acid with acetic acid to decompose the potassium carbonate present. Evaporate to sirupy consistency upon the water-bath and cover the mass with considerable 90 per cent alcohol. By this means the blue coloring matter is precipitated, while the remainder of the violet substance remains in solution with the potassium acetate. Filter off the residue and dissolve it in sufficient hot water so that 3 drops of the solution will be necessary to impart a distinct color to 50 ml of water.

Use. — Litmus can be used for the titration of inorganic and strong organic acids, alkali and alkaline-earth hydroxides, and ammonia, as well as for the titration of carbonates in hot solution. Keep the in-

* *Lehrbuch der chemisch-analytischen Titrirmethoden.*

dicator solution in bottles with a stopper loosely plugged with cotton. Mold forms in a tightly stoppered bottle and the indicator is spoiled.

Choice of Indicators in Titrations. — The titration of an acid with a solution of a base is generally called a neutralization, but a sharp end point is obtained at $p_H = 7$ only when the acid and base are both strong electrolytes. If the acid and base are equally strong, the end point should occur at $p_H = 7$ but it will not be sharp. This is illustrated by the plotted curves on p. 484. The titration of a weak acid with a weak base should be avoided whenever possible because of this difficulty in getting a sharp end point.

The curve on p. 484 for the titration of hydrochloric acid with sodium hydroxide shows that the titration is practically finished at p_H = about 3.5 and the next drop of 0.1 N sodium hydroxide solution changes the p_H to about 10.5. In reading such a curve, the true end point is taken half-way up the nearly vertical line, which is at $p_H = 7$ in this case. Any indicator that changes color between $p_H = 3.5$ and $p_H = 10.5$ should give a good result.

The curve for the titration of acetic acid with sodium hydroxide shows that the end point is at about $p_H = 9$. Such a solution is alkaline because of the hydrolysis of sodium acetate. In this titration, therefore, the end point is not at the neutral point but it occurs at what is sometimes called the *equivalence point, i.e.*, when a quantity of sodium hydroxide *equivalent* to the acetic acid present has been added. A study of the curve shown on p. 484 shows that methyl orange which changes color at $p_H = 2.9$–4.0 is absolutely useless for this titration, but phenolphthalein which changes color at $p_H = 8.3$–10 should give a good result. A similar study of the titration of ammonia with hydrochloric acid will show that phenolphthalein is useless and that methyl red or methyl orange can be used. From the ion product constant of water and the ionization constant of the weak acid or base to be titrated, it is possible to compute the p_H value of the solution at the equivalence point, and when this is known the proper indicator can be chosen.

The stronger the acid, the larger the ionization constant. For a completely ionized acid, the ionization constant is assumed to be 1, cf. p. 483. The mass-action law does not help us much when the ionization is practically complete. When expressing concentrations in moles per liter we assume that one unit of a binary electrolyte gives two, and this leads to a mathematical error because the units are not absolutely the same. Such an error, however, can be disregarded in working with weak electrolytes.

In considering the ionization of acids with more than one replaceable hydrogen, such as sulfuric or phosphoric acid, the ionization reactions should never be written $H_2SO_4 \rightleftarrows 2\ H^+ + SO_4^{--}$ or $H_3PO_4 \rightleftarrows 3\ H^+ + PO_4^{---}$ because the first equation states that one sulfate anion is formed for every two hydrogen ions and the second

equation states that one phosphate is formed for every three hydrogen ions. This is false. The ionization takes place in two stages in the case of sulfuric acid and in three stages in the case of phosphoric acid

$$H_2SO_4 \rightleftarrows H^+ + HSO_4^- \qquad H_3PO_4 \rightleftarrows H^+ + H_2PO_4^-$$
$$HSO_4^- \rightleftarrows H^+ + SO_4^{--} \qquad H_2PO_4^- \rightleftarrows H^+ + HPO_4^{--}$$
$$HPO_4^{--} \rightleftarrows H^+ + PO_4^{---}$$

The corresponding mass-action expressions are

$$\frac{[H^+][HSO_4^-]}{[H_2SO_4]} = K_1 = [1] \qquad \frac{[H^+][H_2PO_4^-]}{[H_3PO_4]} = K_1 = 1.1 \times 10^{-2}$$
$$10^{-2} \qquad \frac{[H^+][HPO_4^{--}]}{[H_2PO_4^-]} = K_2 = 2.0 \times 10^{-7}$$
$$\frac{\quad ^{--}]}{]} = K_3 = 3.6 \times 10^{-13}$$

In the case of phosphoric acid, we may consider that three acids are present. The first acid, H_3PO_4, corresponds to a moderately strong acid and is about 35 per cent ionized in tenth-normal solution; the second acid is weak and will not show an acid reaction to methyl orange; the third is an extremely weak acid. We can multiply the three equilibrium expressions together and get $\frac{[H^+]^3 \times [PO_4^{---}]}{[H_3PO_4]} = K_1 \times K_2 \times K_3 = 7.2 \times 10^{-21}$, which is precisely the same form of expression that we would get if the reaction $H_3PO_4 \rightarrow 3\ H^+ + PO_4^{---}$ took place, but in substituting numerical values we should have $[H^+]$ that obtained by the primary ionization because the quantities of H^+ formed by the secondary and tertiary ionization are inappreciable with respect to that formed by the primary ionization. The value of $[PO_4^{---}]$ would be merely that extremely low concentration formed by the tertiary ionization. The only significance of the expression $K_1 \times K_2 \times K_3$ is to show the effect that increasing the H^+ concentration has upon that of the PO_4^{---}. This explains, for example, why phosphates dissolve readily in solutions of HCl or HNO_3.

The following table shows the ionization constants of some acids and bases.

Acids		K_a	$p_a = -\log K_a$
Acetic		1.8×10^{-5}	4.74
Arsenic, K_1		5.0×10^{-3}	2.30
Benzoic		6.8×10^{-5}	4.16
Boric		6.0×10^{-10}	9.22
Carbonic	K_1	3.0×10^{-7}	6.52
	K_2	7.0×10^{-11}	10.16
Citric	K_1	8.0×10^{-4}	3.10
	K_2	5.0×10^{-5}	4.30
	K_3	2.0×10^{-6}	5.70
Chromic, K_1		6.0×10^{-7}	6.22
Formic		2.0×10^{-4}	3.70
Hydrogen cyanide		7×10^{-10}	9.14
Hydrogen sulfide	K_1	9×10^{-8}	7.05
	K_2	1.2×10^{-15}	14.92
Phosphoric	K_1	1.1×10^{-2}	1.96
	K_2	2.0×10^{-7}	6.70
	K_3	3.6×10^{-13}	12.44

Acids	K_a	$p_a = -\log K_a$
Oxalic K_1	3.8×10^{-2}	1.42
Oxalic K_2	3.5×10^{-5}	4.46
Sulfuric, K_2	3.0×10^{-2}	1.52
Sulfurous K_1	1.7×10^{-2}	1.77
Sulfurous K_2	1.0×10^{-7}	7.00
Tartaric K_1	9.7×10^{-4}	3.01
Tartaric K_2	9.0×10^{-5}	4.05
Trichloroacetic	1.3×10^{-1}	0.88
Bases	K_b	$p_b = -\log K_b$
Ammonia	1.75×10^{-5}	4.76
Barium hydroxide, K_2	3×10^{-2}	1.52
Hydrazine	3.0×10^{-6}	5.52
Ethylamine	5.6×10^{-4}	3.25

As stated above, the reason why the end point is not at $p_H = 7$ in titrating a weak acid with a strong base or a weak base with a strong acid, is because the salt is hydrolyzed to an appreciable extent. When the end point is reached, the solution should have the p_H caused by the quantity of salt formed in the total volume of solution.

The hydrolysis of a salt can be expressed as follows:

$$BA + H_2O \rightleftharpoons BOH + HA$$

when BA represents the formula of the salt, BOH that of the base, and HA that of the acid. Since most salts, excepting the halides of mercury and cadmium, are almost completely ionized in dilute aqueous solutions, this hydrolysis equation becomes

$$A^- + H_2O \rightleftharpoons OH^- + HA \tag{1}$$

when BOH is a strong electrolyte and HA is a weak acid. The mass-action law applied to this reaction of hydrolysis is

$$\frac{[OH^-] \times [HA]}{[A^-]} = K_{\text{hydr.}} \tag{2}$$

The quantity of water involved in the reaction is very small as compared with the total quantity of water in the solution so that $[H_2O]$ is regarded as a constant quantity and is left out of the mass-action law expression.

Now if we multiply equation (2) by $\dfrac{[H^+]}{[H^+]}$

$$\frac{[H^+] \times [OH^-] \times [HA]}{[H^+] \times [A^-]} = \frac{K_w}{K_a} = K_{\text{hydr.}} \tag{3}$$

Now according to equation (1) an equal quantity of OH^- and HA are formed by the hydrolysis so that in equation (2) we can replace [HA] with $[OH^-]$, and since the salt formed is practically completely ionized we can replace $[A^-]$ with c, the concentration of the salt present in the solution after the hydrolysis has taken place. This gives us

$$\frac{[OH^-]^2}{c} = \frac{K_w}{K_a} = K_{\text{hydr.}} \tag{4}$$

and

$$[OH^-] =$$

Using logarithms we have

$$\begin{aligned}\log [OH^-] &= \tfrac{1}{2}\log K_w + \tfrac{1}{2}\log c - \tfrac{1}{2}\log K_a \\ &= -7 + \tfrac{1}{2}\log c + \tfrac{1}{2}\, p_a\end{aligned}$$

because $\log K_w = -14$ and $-\log K_a = p_a$.

Then by changing all the signs, the equation becomes

$$-\log [OH^-] = p_{OH} = 7 - \tfrac{1}{2}\log c - \tfrac{1}{2}\, p_a$$

and since, $p_H + p_{OH} = 14$, and $p_H = 14 - p_{OH}$, the formula for computing p_H at the equivalence point in titrating a *weak acid with a strong base* is

$$p_H = 7 + \tfrac{1}{2}\log c + \tfrac{1}{2}\, p_a$$

Precisely the same line of reasoning leads us to the formula for the equivalence point in the titration of *a weak base with a strong acid*

$$p_H = 7 - \tfrac{1}{2}\log c - \tfrac{1}{2}\, p_b$$

These last two equations enable one to choose the proper indicator for the titration of a weak acid or a weak base of which the ionization constant is known. The indicator chosen should change color at the p_H indicated for the equivalence point.

It is sometimes possible to titrate a mixture of two acids in such a way that the quantity of each acid present is known. This is accomplished by using two indicators. With equal initial concentrations of the two acids it is possible to titrate each separately with an accuracy of less than 1 per cent if the ionization constants are to one another as 10,000 : 1 or, in other words, if the difference in the ionization constants is at least 10^{-4}. If there is 100 times as much of one as of the other, there must be a difference of 10^6 in the constants. Thus it is possible to titrate hydrochloric acid in the presence of boric acid or hydrochloric acid in the presence of acetic acid. In the same way it is possible to titrate carbonate in the presence of bicarbonate; the two ionization constants of carbonic acid are 3×10^{-7} and 7×10^{-11}, respectively. Phenolphthalein shows when the carbonate is converted into bicarbonate and methyl orange shows when all the bicarbonate has reacted with a strong acid like hydrochloric. The ionization constants of phosphoric acid are $K_1 = 1.1 \times 10^{-2}$, $K_2 = 2.0 \times 10^{-7}$, and $K_3 = 3.6 \times 10^{-13}$. Methyl orange shows when the first end point is reached, and phenolphthalein indicates the second. An indicator changing at $p_H = 14$ will give a fair idea of when the third hydrogen has all reacted, but this third hydrogen is present to such an extremely slight extent that the end point is not sharp.

As the curves on p. 484 show, the progress of the neutralization of an acid by a base in dilute solution can be followed electrometrically and by potentiometric measurements the p_H can be determined at which any given indicator changes color in aqueous solution. In Vol. I it was shown in the discussion of Electromotive Series and Oxidation Potentials that an electromotive force results when a metal is placed in contact with a solution of its ions and that this potential difference can be expressed mathematically by means of the Nernst formula,

$$E_{18^\circ} = \frac{0.058}{n}\log\frac{P}{p}$$

in which $E_{18°}$ represents the electromotive force at 18°, or the approximate laboratory temperature,* n is the valence of the ion, P is the electrolytic solution tension, which has a constant value for any given metal, and p is the osmotic pressure. This Nernst formula shows the influence of the osmotic pressure, which is proportional to the concentration, upon the electromotive force developed; the more dilute the solution, the smaller becomes the value p and the greater the value of $E_{18°}$. An electrolytic cell is developed whenever two different metals differing in solutions of their respective ions are used as electrodes as in the Daniell cell, or when the electrodes are the same metal dipping in solutions of different concentration. Thus if metallic silver, as anode, is dipped into 0.01 N silver nitrate solution which is separated by a porous cell from 0.1 N silver nitrate and another silver electrode as cathode, a current will flow on connecting the electrodes externally and the electromotive force will be approximately 0.058 volt at 18°. This is evident from the Nernst formula because the factors are all the same in developing the values of $E_{18°}$ at each electrode except the value p which has a tenfold increase in the concentrated solution corresponding to a difference of 1 in the logarithm.

If a hydrogen electrode (an S-shaped platinum electrode covered with platinum black and kept saturated with hydrogen gas) is placed in a solution together with an electrode of known electromotive force such as a calomel electrode, and the electrodes are connected externally, a current will flow if there is any difference in potential between the hydrogen electrode and the standard electrode. The voltage can be measured by sending a current from a dry cell in the opposite direction and measuring the voltage of this second current when it just suffices to neutralize the original current.

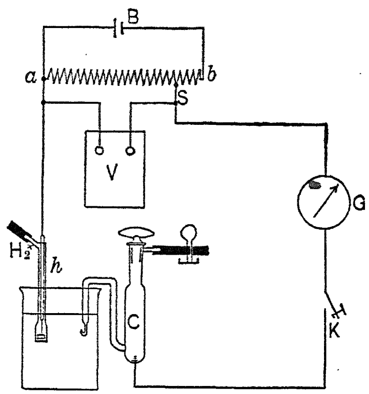


FIG. 108.

Figure 108 is a diagram of such an arrangement as used by Hildebrand.† A beaker contains the hydrogen electrode h and the calomel electrode C; the latter is connected through the switch K with the galvanometer G and thence to the positive pole of the dry cell B. By means of the

* If the measurements are made at 25°, the formula is the same except that the value 0.058 becomes 0.0591.

† *J. Am. Chem. Soc.*, **35**, 847 (1913).

sliding contact S, a variable fraction of the current can be made to pass from the dry cell through a galvanometer to the calomel electrode, opposing the current which results from the potential difference between the two electrodes in the solution. When the two emf's are equal, no current flows in the wire, as shown by the needle of the galvanometer, and the voltage can be read at V.

The Nernst equation, applied to the equilibrium between hydrogen gas and hydrogen ions becomes $E_{18°} = 0.058 \log \frac{1}{c}$, which means that the potential of the hydrogen electrode against a solution can be used to measure the hydrogen-ion concentration of the solution. The expression $\log \frac{1}{c}$ when c is the concentration of the hydrogen ions expressed in moles per liter (or normality in this case) is called the p_H value of the solution (cf. p. 155).

Standardization of Acids and Bases

There are many excellent ways in which a solution of hydrochloric acid can be standardized with satisfactory accuracy. The standardization can be accomplished gravimetrically by taking a measured volume of the acid from a pipet or buret, diluting with water, adding a slight excess of silver nitrate, heating to coagulate the precipitate, filtering, and weighing the silver chloride precipitate. Such a procedure corresponds to the determination of chlorine in a sample of sodium chloride to be described later.

The acid solution can be standardized by measuring the volume required to react with a pure substance of definitely known chemical composition. A satisfactory standard is sodium carbonate prepared by heating pure sodium bicarbonate to 270°. Gay-Lussac recommended this method early in the nineteenth century. Other standards such as calcite (Grandeau and also Pincus in 1863), potassium bicarbonate (Ure, 1839), sodium bicarbonate (North and Blakey, 1905), potassium bitartrate (Borntraeger, 1892), which is first converted into potassium carbonate by heating strongly, sodium oxalate (Sörensen, 1893), which is converted into sodium carbonate by ignition, and borax (Salzer and also Rimbach in 1893) have all been shown to give good results. In many cases it is convenient to standardize the acid against a solution or base which has itself been standardized. This last procedure is called the *indirect method.*

There is no good gravimetric method for standardizing a solution of sodium hydroxide, but numerous pure substances have been recommended as standards. Pure oxalic acid crystals, $H_2C_2O_4 \cdot 2H_2O$, were used by Fr. Mohr in 1852, and since then the following are only a few of the acids or acid salts which have been advocated: potassium acid oxalate, KHC_2O_4; potassium tetroxalate, $KHC_2O_4 \cdot H_2C_2O_4 \cdot 2H_2O$; succinic acid, $C_2H_4(CO_2H)_2$; potassium bi-iodate, $KH(IO_3)_2$; benzoic acid, $C_6H_5CO_2H$; potassium acid phthalate, $KHC_8H_4O_4$. An indirect method of standardizing sodium hydroxide solution is the titration against a solution of acid which has been standardized.

In this book only two methods of standardizing the hydrochloric acid will be described and two methods for standardizing the sodium hydroxide. The student

may choose one of these and then determine the strength of his other solution indirectly, using the results that he has already obtained by titrating the hydrochloric acid against the sodium hydroxide.

Standardization of Acid against Sodium Carbonate

Preparation of the Standard. — If pure sodium bicarbonate is not available, dissolve about 35 g of the commercial product in 350 ml of warm water and filter off any insoluble residue. Allow the water to evaporate slowly at a temperature of not over 40° until about 25 g of salt has deposited. Protect the solution from contamination by dust by covering it with a watch glass supported upon a glass triangle or glass supports. Finally pour off the mother-liquor; dry the crystals by pressing them between filter papers and by heating for an hour at 120°. Preserve the pure sodium bicarbonate in a glass-stoppered bottle.

Place about 8 g of pure sodium bicarbonate in a platinum or porcelain crucible and heat for 30 minutes at a temperature of about 270°, taking care that the temperature does not rise above 300°. The heating can take place in an electric oven, in a sand-bath, or in an air-bath.

If a sand-bath is used, embed the crucible so that the sand on the outside is level with the sodium bicarbonate on the inside. Occasionally stir the contents of the crucible with a 360° thermometer. After heating for half an hour, allow the crucible and its contents to cool in a desiccator over calcium chloride or other suitable desiccant. Preserve the sodium carbonate in a glass-stoppered weighing-bottle. If exposed to the air or kept in a cork-stoppered bottle it soon absorbs water from the atmosphere and becomes worthless as a standard.

Standardization. — To standardize 0.5 N hydrochloric acid, weigh out two separate portions of about 1 g, recording the weight to the nearest tenth of a milligram.

Dissolve the weighed portions of pure sodium carbonate in about 100 ml of distilled water, add some methyl orange indicator, and titrate the cold solution with the hydrochloric acid solution until the color of the solution, after it has been stirred well, begins to change from yellow to red. Or, with phenolphthalein as indicator, add an excess of acid, boil gently till all carbon dioxide is removed, cool, and titrate the excess acid with sodium hydroxide solution. Then, if the relative strengths of the acid and base are determined by titration with the same indicator, the concentration of both solutions can be computed. The equivalent weight of sodium carbonate is 53.00.

Standardization with Sodium Oxalate. — Sörensen prefers to weigh out pure sodium oxalate, such as can be obtained from the Bureau of Standards, and to convert the weighed sample to sodium carbonate.

In this case it makes no difference if a little carbon dioxide is lost. Weigh out the standard oxalate, after suitable drying to remove hygroscopic moisture, and heat it very carefully in an air-bath (p. 37). A slight carbonization does no harm, but this should be avoided by keeping the temperature low and raising the temperature gradually. It is well to heat first for an hour at 270° in an electric oven. Finally, after there is no more danger of mechanical loss being caused by the escaping carbon monoxide, raise the temperature to about 500°. Cool, dissolve in water and titrate the sodium carbonate solution as described above.

$$Na_2C_2O_4 = Na_2CO_3 + CO$$

If the product is very black, moisten it with water, evaporate carefully and again heat.

The milli-equivalent of sodium oxalate is 0.06700 g.

Standardization of Sodium Hydroxide

(a) *With Potassium Acid Phthalate*

This substance, because of its high molecular weight, is particularly well suited for the standardization of dilute solutions of sodium hydroxide. To standardize 0.1 N sodium hydroxide, about 1 g of the salt should be taken, as this is sufficient to neutralize 49 ml of the base. Phenolphthalein is a suitable indicator, but reliable results cannot be obtained with methyl orange. The chief difficulty that students have in working with phenolphthalein arises from the fact that the sodium hydroxide absorbs a little carbon dioxide from the air every time the storage bottle is opened, unless care is taken to prevent it. This can be prevented by pumping the sodium hydroxide into the buret, or by siphoning it from the storage bottle, in such a way that all air that enters the bottle has to pass through a tube containing soda-lime ($Ca(OH)_2 + NaOH$) or ascarite (a patented preparation of asbestos fibers impregnated with sodium hydroxide). It also helps to keep the solution under a layer of gasoline. Every molecule of carbon dioxide that combines with two molecules of sodium hydroxide to form sodium carbonate, yields a product that only reacts with one molecule of hydrogen chloride in the cold because the sodium bicarbonate, which is formed when one molecule of hydrochloric acid acts on one molecule sodium carbonate, is neutral to phenolphthalein. The resulting error can be overcome by boiling the acid solution to expel carbon dioxide and repeating the process if the phenolphthalein color of the neutralized solution is discharged by heating. If the ratio of acid to base has been determined with methyl orange as indicator, the presence of carbonate in the sodium hydroxide solution will be detected by determining the ratio with phenolphthalein as indicator. The sodium hydroxide solution will prove weaker when phenolphthalein is used if it contains carbonate and the titration is carried out in the cold.

Procedure. — To standardize 0.5 N sodium hydroxide, weigh out portions of potassium acid phthalate weighing 2.5–3.0 g into 200-ml Erlenmeyer flasks. Record the weight to the nearest milligram. Add 100 ml of water to each portion and shake gently until all the solid has

dissolved. Add 3 drops of phenolphthalein solution and titrate till a pale pink color is obtained. Heat the solution to boiling and, if the color fades, add more of the sodium hydroxide solution until the color persists after boiling for 30 seconds. The equivalent weight of potassium acid phthalate is the molecular weight, 204.1. Compute the normal concentration of the base, and, from the ratio of acid to base previously found, compute the normal concentration of the hydrochloric acid solution as well.

For the most accurate work, the solution of sodium hydroxide must be prepared free from carbonate, the water used for dissolving the standard must have been recently boiled to remove carbon dioxide, the titration must take place in a flask which has been swept free from carbon dioxide by passing through it a stream of air that has been made to flow through granular soda-lime or ascarite, and a blank test must be run under the same conditions to see how much sodium hydroxide would have been used if no potassium acid phthalate had been present. The volume used in the blank test must be deducted from that used in the standardization.

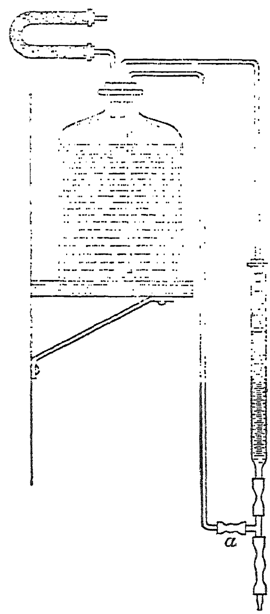


FIG. 109.

(b) *With Benzoic Acid*

Weigh out 1.5–2.0 g portions of the pure acid into 200-ml flasks and record the weights to the nearest milligram. Add 40 ml of alcohol, stopper the flask and allow to stand until the acid has all dissolved. Add 3 drops of phenolphthalein indicator, dilute with water to 100 ml and titrate with the 0.5 N sodium hydroxide. When a slight pink color is obtained, heat the solution and see if the color disappears. If so, add more sodium hydroxide until the color is not bleached by boiling for 30 seconds. Run a blank test with the same quantities of water and alcohol and deduct the volume of sodium hydroxide required in this test from the total volume used in the standardization.

Everything that was said under (*a*) concerning the effect of carbon dioxide is true here. Sodium hydroxide free from carbonate can be prepared by adding about 20 ml of 0.5 N barium chloride to the sodium hydroxide solution. Allow the precipitate of barium carbonate to settle, stopper the bottle with a two-hole rubber stopper carrying a short right-angled tube attached to a soda-lime tube through which air can enter the bottle and also carrying a siphon tube reaching nearly to the bottom of the bottle. Then place the bottle on a shelf above the buret and siphon

the solution into the buret as required. See Fig. 109. The valve at *a* is made by a round bead in the rubber tubing.

(c) *With Constant-boiling Hydrochloric Acid**

This method will not be described in detail but deserves mention because it is one of the most accurate methods for standardizing dilute solutions of alkali hydroxides. Briefly it consists in distilling hydrochloric acid until a constant boiling acid of sp. gr. about 1.1 is obtained. The exact density and composition of this constant-boiling acid varies slightly with the barometric pressure that prevails during the distillation. Thus with a barometer reading of 730 mm the acid will contain 20.293 per cent of hydrogen chloride, and at 770 mm the acid will contain 20.197 per cent of hydrogen chloride. These values are on a vacuum weight basis.

After about three-quarters of approximately 6 *N* hydrochloric acid have been distilled off, the next 10 to 15 per cent of the distillate is collected as the standard acid. During this last distillation, the barometer is read at the start and finish to the nearest millimeter. Then, for the analysis, portions of the acid are weighed from a weight buret (see Fig. 107, p. 471). The method is very exact but is not suitable for work with large classes during a brief course in quantitative analysis.

Normal Hydrochloric Acid

1000 ml contain 36.47 g of HCl

Dilute pure, concentrated hydrochloric acid of the laboratory with 11 volumes of water. In this way a solution is obtained that is slightly more than normal in strength. To obtain an exactly normal solution, titrate it against a weighed amount of chemically pure sodium carbonate, and from the result obtained compute the volume of water to be added.

In the standardization of any volumetric solution it is advisable to take a weight of substance such that the titration can be accomplished with one filling of the 50-ml buret and heavy enough so that the normal titration error will not amount to more than 0.001 of the total volume of standard solution used. This is accomplished by taking enough substance to react with 35–40 ml of the solution to be standardized. It is always well to run a blank with the water used, to see how much of the solution is required to give an end point similar to that used in the analysis. The blank titration should have the same volume of water, the same amount of indicator and the same temperature as the main solution, and in working with methyl orange it is best to match the shades.

To standardize the acid, proceed as directed on pp. 499–500. Of pure sodium carbonate, use about 2 g for a normal solution; add 100 ml

* Foulk and Hollingsworth, *J. Am. Chem. Soc.* **45**, 1220 (1923); Hulett and Bonner, *Ibid.*, **31**, 390 (1909); Bonner and Branting, *Ibid.*, **48**, 3093 (1926).

of water and 2 drops of methyl orange indicator solution. Start the titration at approximately the zero-reading of the buret. Record the reading in the notebook, estimating to the nearest hundredth of a milliliter. Titrate slowly with constant stirring until the color changes from yellow to orange. With a little practice it is easy to tell when the end point is nearly reached by the fact that a pink color is produced which fades slowly on stirring. Finally, at the right end point, the color changes from yellow to orange throughout solution. It is advisable to match the color with that obtained by adding the indicator solution to pure water and adding just enough acid to give an orange tint to the solution.

If the end point is over-stepped, add enough standard sodium hydroxide (p. 505) to restore the yellow color and finish with acid again. Titrate the sodium hydroxide against the acid as described on p. 505.

Computation. — If no sodium hydroxide is used the computation is very simple. By definition, 1 ml of normal acid reacts with 1 milli-equivalent of sodium carbonate (molecular weight 106.05), or 0.05303 g of Na_2CO_3. To find the ratio to the normal, or *normality* of the acid, it is only necessary to find out how much sodium carbonate was actually neutralized by 1 ml of the acid and divide this value by the milli-equivalent, or *norm*, of sodium carbonate.

Thus if t milliliters of acid were required to neutralize s grams of sodium carbonate, the solution is $\frac{s}{t \times 0.05303}$ normal.

If the end point was over-stepped it is necessary to know the relative strengths of the acid and base used in the titration. Assume that by titration it was found that a milliliters of HCl = b milliliters of NaOH. Then 1 ml NaOH $= \frac{a}{b}$ milliliters of HCl. If in the titration of s grams of sodium carbonate p milliliters of HCl and q milliliters of NaOH were used then $t = p - \frac{a}{b}q$ and the above equation holds. If N_A is the normality of the acid, $N_A \times \frac{a}{b} = N_B$, the normality of the sodium hydroxide.

When many analyses have to be made as a part of the routine work of a commercial laboratory it is convenient to make the solutions of acid and base of exactly the same strength and to keep the solutions always exactly normal, or 0.1 N, or 0.5 N as the case may be. Since it is not practical to concentrate a large volume of solution to a definite volume by evaporation it is advisable to make up the solution so that it is a little stronger than desired. If N is the desired normality and

N' the normality of the solution as first made up, then the solution is $\frac{N'}{N}$ as strong as desired and should be diluted accordingly.

Thus if the solution is $1.023\,N$ it is only necessary to add 23 ml of water to each liter of solution to make it $1\,N$; if it is $0.5012\,N$, add 1.2 ml of water to each 500 ml of solution to make it exactly $0.5\,N$. Measure out the solution in a measuring-flask calibrated for delivery and add the required volume of water from a buret.

Place a label on each standard reagent and write on it the normal concentration with 4 significant figures and the date that the standardization was made. This is desirable because solutions often change on standing as a result of evaporation, the action of the reagent on the glass container or by decomposition as a result of impurities present.

For most purposes a normal solution is too strong, and 0.1 or $0.5\,N$ solutions are more commonly used. Prepare these in exactly the same way but by using correspondingly smaller quantities of reagents. In titrating with $0.1\,N$ solutions it is quite necessary to make allowance for the acid or base required to react with the indicator and important to keep all conditions the same, such as temperature, volume, and quantity of indicator used in duplicate titrations. Alkaline solutions should not be used in burets with a glass stopcock.

All volumetric titrations should be carried out in duplicate. Burets should be rinsed with at least three 10-ml portions of the liquid before filling them. They must be kept clean so that no drops form on the sides as they drain. In using measuring-flasks, they should also be well cleaned (see p. 465) and when used as above, should be rinsed with at least three 25-ml portions of the liquid before filling them.

Normal Nitric and Sulfuric Acid Solutions

These are prepared in the same way as was described in the preparation of normal hydrochloric acid.

0.1 *N* Oxalic Acid

$$1000 \text{ ml contain } \frac{H_2C_2O_4 \cdot 2H_2O}{20} = \frac{126.06}{20} = 6.303 \text{ g}$$

An oxalic acid solution of this strength can be prepared by dissolving exactly 6.303 g of pure, crystallized oxalic acid in water and diluting to a volume of 1 l in a calibrated flask with water at the laboratory temperature, (cf. p. 478). Titrations with this acid should be made with phenolphthalein as indicator.

Normal Sodium Hydroxide Solution

1000 ml contain 1 NaOH = 40.01 g

Dissolve about 45 g of commercial caustic soda in a little more than a liter of water. Allow the solution to stand for about 1 hour beside the hydrochloric acid against which it is to be titrated, in order that both solutions may be at the same temperature. Measure off about 40 ml of the solution from a buret, and titrate with normal hydrochloric acid after the addition of 2 drops of methyl orange solution. The necessary computation was indicated on p. 503.

Titration of Alkali containing Carbonate with Phenolphthalein in Hot Solutions

To the alkaline solution introduce 2 drops of phenolphthalein indicator and add, from the buret, hydrochloric acid of approximately the same strength until the red color disappears. Heat the solution to boiling; the red color soon reappears. Cool by placing the beaker in cold water,* again decolorize with hydrochloric acid, and repeat the process until finally the red color does not reappear on boiling. This method of titration is tedious, but the results obtained are accurate.

On titrating 0.1 *N* acids with methyl orange as indicator, there is no sharp change from yellow to pink, as with normal and half-normal solutions, but first a brownish orange color is obtained which becomes pink on the addition of more acid. The correct end point is the change from yellow to yellowish brown. Only when considerable carbonate is present will this change occur before enough acid has been added, for in this case the carbon dioxide exerts an action upon the methyl orange. The disturbing action of carbon dioxide is best prevented by first titrating in the cold, then heating to remove the carbon dioxide, again titrating the *cold* solution with acid. If only a small amount of carbonate is present, it exerts no appreciable effect upon methyl orange.

The titration of oxalic acid with alkali hydroxide solution which contains carbonate is best effected with phenolphthalein in hot solution. The process is carried out as follows: Measure out about 40 ml of the sodium hydroxide into a beaker, add 2 drops of phenolphthalein, and run in oxalic acid from a buret until the solution is decolorized. Heat the solution upon the water-bath until the red color reappears, decolorize with oxalic acid, and continue the process until finally the color does not reappear on heating the solution. This point is reached, however, only after the solution has been evaporated to dryness and the residue

* With phenolphthalein the titration can be finished in the hot solution, but the end point is not so sharp.

taken up with a few milliliters of distilled water. A slight red color will appear after this first evaporation, but it will be discharged by the fraction of a drop of oxalic acid and will not reappear upon a second evaporation.

Remark. — By heating the solution of oxalic acid over a free flame there is likely to be some decomposition. Sörensen thought that the trouble was caused by the following hydrolysis, $2\ Na_2C_2O_4 + H_2O = Na_2CO_3 + 2\ HCO_2Na + CO_2$, but Treadwell showed that the following reaction takes place when the sides of the containing vessel are overheated, $Na_2C_2O_4 = Na_2CO_3 + CO$.

Preparation of Sodium Hydroxide Solution Free from Carbonate

This is best effected as proposed by Küster.* Place about 40 ml of pure alcohol in a small round-bottomed flask, heat to boiling on the water-bath, and add little by little 2.5 g of bright metallic sodium, freed from petroleum by rubbing between pieces of blotting-paper. The reaction between the boiling alcohol and the sodium is at first very violent and large amounts of hydrogen and alcohol vapors are evolved. During this time keep the flask covered with a watch glass. Gradually the reaction begins to diminish and finally stops. In the flask there will be a deposit of sodium alcoholate and some undissolved sodium on account of the insufficient amount of alcohol. Add small quantities of water free from carbon dioxide† a test-tube full at a time. Boil off most of the alcohol and, in order to remove it completely, pass a current of air free from carbon dioxide through the solution until the odor of alcohol can no longer be detected. Cool quickly, adding cold water free from carbon dioxide, immediately place in a liter flask, and dilute to the mark with pure water at 17–18°. This solution will give the same value when titrated with phenolphthalein in a cold solution as when the latter is hot.‡ With methyl orange correct results are obtained cold if the orange color is taken as the end point.

Such a solution quickly absorbs carbon dioxide from the air. In order to prevent this, place it in a bottle as shown in Fig. 109, p. 501, which is connected with a soda-lime tube, *N*, and with the buret by means of the tubes *p* and *r*. The buret is filled through the valve at *a*. In this way a solution can be kept free from carbon dioxide for a long time. To determine whether the solution is free from carbonate, make

* *Z. anorg. Chem.*, **13**, 134 cf. p. 501.

† Pass air, freed from carbon dioxide by a soda-lime tube, through the boiling water.

‡ Provided the hydrochloric acid solution was prepared with water free from carbonate, otherwise too little acid will be necessary when the titration takes place in the cold.

two parallel titrations with phenolphthalein as an indicator, one in the cold and the other in the hot solution. If the results agree the solution is free from carbonate. Otherwise it is necessary to prepare a fresh solution or to make a corresponding correction in each analysis after determining the amount of carbonate present as described on p. 510.

In many cases it is better to use a 0.1 N barium hydroxide solution; as long as it remains clear it is free from carbonate.

Preparation of 0.1 N Barium Hydroxide Solution

$$1000 \text{ ml contain } \frac{Ba(OH)_2 + 8\,H_2O}{20} = \frac{315.51}{20} = 15.78 \text{ g}$$

The crystallized barium hydroxide of commerce always contains barium carbonate, so that the solution cannot be prepared by simply weighing out the necessary quantity and diluting to 1 l. Dissolve about 20 g of the commercial hydroxide in the necessary amount of distilled water within a large flask. Close the flask and shake until the crystals have completely disappeared and a light, insoluble powder of barium carbonate remains. Allow the solution to stand for 2 days, until the barium carbonate has completely settled; siphon it off into a bottle through which a current of air free from carbon dioxide has been passed for 2 hours previous. Connect this bottle with a soda-lime tube and with a buret as shown in Fig. 109, p. 501. For the titration, place 50 ml of 0.1 N hydrochloric acid in an Erlenmeyer flask, add a little phenolphthalein, and titrate with the barium hydroxide solution. The normality found should be written upon the label. It is not advisable to make the solution exactly 0.1 N, for it usually becomes turbid on diluting.

A. Alkalimetry

1. Determination of Alkali Hydroxides

Rule. — If the substance to be analyzed is a solid, dissolve an accurately weighed quantity in enough water to make the solution of about the same concentration as that of the acid to be used in the titration. If a solution of an alkali hydroxide in water is to be analyzed, determine the specific gravity of the solution, then dilute accordingly.

(a) Determination of Sodium Hydroxide in Commercial Caustic Soda

For the titration 0.5 N hydrochloric acid solution can be used. As sodium hydroxide absorbs carbon dioxide from the air it is difficult to

get a good sample. Place the material in a weighing-beaker and weigh out a sample of 4–6 g into a liter measuring-flask. Dissolve in water that has been freed from carbon dioxide (p. 506), and dilute the cold solution up to the mark. Mix, measure out 100-ml aliquot portions for the titration with methyl orange as indicator.

Computation. — If 5.001 g were taken for analysis and in the titration of the aliquot 24.18 ml of 0.5 N acid were used, the percentage purity of the sample can be computed as follows:

$$1 \text{ ml of } 0.5\,N \text{ HCl} = 0.02000 \text{ g NaOH } (\text{NaOH} = 40.01)$$

Therefore,

$$\frac{24.18 \times 0.02000 \times 100}{0.5001} = 96.72 \text{ per cent NaOH}$$

In this particular case, note that the volume of NaOH solution used is exactly one-fourth the percentage of pure NaOH present. This is because the weight of sample in the aliquot (0.5001 g) was 25 times the value of 1 ml of 0.5 N acid in terms of NaOH. The practice of using an original weight such that the final computation can be done mentally is very common in commercial work.

(*b*) *Determination of Sodium Hydroxide Present in Caustic Soda Solution*

Assume caustic alkali solution of *d.* 1.285 is to be analyzed. The table in the back of this book shows that the solution should contain 25.8 per cent of NaOH by weight. One milliliter of solution should contain $1.285 \times 0.258 = 0.3315$ g NaOH.

If it is desired to know the percentage by weight of sodium hydroxide (or its equivalent, as base) present, weigh out about 3 g of solution into a small beaker, add 50 ml of water, and titrate with 0.5 N alkali using methyl orange as indicator.

If it is desired to know the weight of NaOH per milliliter, measure out 25 ml of the caustic soda solution, dilute with water at the laboratory temperature to 1000 ml, mix, and use 100 ml for the titration.

Remark. — The titration of alkali hydroxides with methyl orange as an indicator will only give correct results when the alkali hydroxide is free from carbonate, which with commercial material is never the case. The above results are too high, for they represent the total amount of alkali, *i.e.*, the amount of $NaOH + Na_2CO_3$, though the latter is expressed in terms of NaOH. For an accurate determination of alkali hydroxide in the presence of alkali carbonate, see pp. 510, 512.

(*c*) *Determination of Ammonia in Aqueous Ammonia*

The procedure is the same as under (*b*).

(d) *Determination of Ammonia in Ammonium Salts*

Weigh out 1 to 2 g of the ammonium salt in the flask K (Fig. 31, p. 75),* dissolve in about 200 ml of water, and treat with 10 ml of a boiled solution of 10 per cent caustic soda. Distil until no more NH_3 is being evolved, as shown by testing 10 ml of the last distillate with litmus or turmeric paper, and receive the distillate in a known volume of 0.5 N acid in the receiver V, as described on p. 75, or in a saturated solution of boric acid. In the latter case the boric acid prevents volatilization of NH_3 from the receiver but it is too weak an acid to affect the indicator in the following titration. Titrate the excess of acid with 0.5 N caustic alkali, using methyl orange or methyl red as an indicator if a known volume of mineral acid was used in the receiver, or the ammonium borate with 0.5 N HCl if boric acid was used.

Computation. — 17.03 g of commercial ammonium sulfate were dissolved in 500 ml of water and one-tenth of the solution (1.703 g) placed in the flask. The distillate was caught in 60 ml of 0.5 N HCl and the excess of acid reacted with t milliliters of 0.5 N NaOH. Since the equivalent weight of NH_3 is 17.03 there is present

$$\frac{(60 - t)\ 0.008515 \times 100}{1.703} = \frac{60 - t}{2} = \text{per cent } NH_3$$

(e) *Titration of Pyridine Bases*†

1000 ml N acid = C_5H_5N = 79.05 g pyridine

The pyridine bases are so weak that they cannot be titrated with ordinary indicators. If, however, an aqueous pyridine solution is treated with an aqueous solution of ferric chloride, the iron is precipitated as ferric hydroxide:

$$FeCl_3 + 3\ C_5H_5N + 3\ HOH = 3\ (C_5H_5N, HCl) + Fe(OH)_3$$

If normal sulfuric acid is very carefully added with constant stirring until the precipitate redissolves, each milliliter of the acid required will correspond to $\frac{C_5H_5N}{1000} = 0.07905$ g pyridine.

Procedure. — Dissolve 5 ml of pyridine in 100 ml of water, treat 25 ml of the resulting solution with 1 ml of 5 per cent aqueous ferric chloride solution, and titrate the precipitate of reddish brown ferric hydroxide with normal sulfuric acid until completely dissolved.

* Or better, the apparatus shown in Fig. 92, p. 403, can be used.

† K. E. Schulze, *Ber.*, **20**, 3391 (1887).

2. Determination of Alkali Carbonates

Alkali carbonates can be titrated in the cold by using methyl orange as an indicator, the end point being taken as the change from yellow to reddish orange. When fifth-, half-, and normal acids are used this is the correct end point, but with tenth-normal acids this change is obtained a little too soon, for large amounts of carbonic acid exert a slight action upon the indicator. In this case the difficulty is best overcome by titrating the solution until the orange color is obtained, then heating to boiling to expel the carbon dioxide, cooling, and again titrating until the now yellow solution becomes orange again.* With phenolphthalein, accurate results may be obtained by titrating the hot solution (cf. p. 505). According to Warder,† sodium bicarbonate solution reacts neutral toward phenolphthalein in the cold, so that when a sample of sodium carbonate is titrated in the cold, with phenolphthalein as an indicator, an end point is obtained when the carbonate is changed to bicarbonate:

$$Na_2CO_3 + HCl = NaCl + NaHCO_3 \ddagger$$

If the acid is allowed to run upon the carbonate solution, a part of the carbon dioxide from the sodium bicarbonate is likely to be lost, so that too much acid must be added before the end point is reached. On the other hand, correct results may be obtained if the titration is carried out slowly at 0° in the presence of NaCl (cf. p. 491) and with the solution gently and continuously stirred to prevent local concentration of the acid. This is important, for in this way a convenient method is obtained for determining the amount of hydroxide in the presence of carbonate.

Analysis of Soda Ash

Soda ash is the trade name for anhydrous sodium carbonate. The following procedure is applicable to the analysis of any alkali carbonate. It can also be used for an alkaline-earth carbonate but in that case it is necessary to add an excess of acid and titrate back with sodium hydroxide solution. As we have seen in the discussion of indicators, carbonic acid is such a weak acid that it has practically no effect upon methyl orange. The primary ionization of carbonic acid, however, furnishes hydrogen ions sufficient to make phenolphthalein assume its colorless form. With methyl orange as indicator, sodium carbonate Na_2CO_3 can be titrated as if it were

* Küster recommends in titrating carbonates with methyl orange, to make a blank experiment to see how much effect an equal amount of water saturated with carbon dioxide has upon the same amount of indicator solution. (*Z. anorg. Chem.*, **13**, 140.)

† *Z. anal. Chem.*, **21**, 102 (1892).

‡ *Z. anorg. Chem.*, **13**, 140.

two molecules of sodium hydroxide, both stages of the following decomposition taking place before the solution is acid to methyl orange:

$$CO_3^{--} + H^+ \rightarrow HCO_3^-$$
$$HCO_3^- + H^+ \rightarrow H_2O + CO_2$$

With phenolphthalein in the cold, an end point is obtained when the first stage only has taken place.

With an insoluble alkaline-earth carbonate, on the other hand, the carbonate does not begin to dissolve until the solution is more acid than corresponds to the first end point, so that a mixture of soluble $Ba(OH)_2$ and insoluble $BaCO_3$ can be titrated with acid and an end point obtained as soon as the $Ba(OH)_2$ has been completely neutralized provided phenolphthalein is the indicator. With methyl orange, on the other hand, the end point will not be reached until all the insoluble carbonate has dissolved.

Procedure. — Weigh out into 250-ml Erlenmeyer flasks, two samples of about 1 g each. Record the weights to four significant figures.* Fill a glass-stoppered buret with standardized hydrochloric acid and a plain buret with standardized sodium hydroxide. Record the initial readings in the notebook to the nearest 0.01 ml.

Cover the sample with 25 ml of water and add 2 drops of methyl orange indicator solution. Run in acid slowly until the indicator turns distinctly red, rotating the contents of the flask. In the case of an insoluble carbonate, it will be necessary to add a few milliliters of excess acid. When all the carbonate is decomposed, wash down the sides of the flask and carefully add sodium hydroxide from the buret while keeping the liquid in the flask in motion. Stop adding the hydroxide as soon as the liquid becomes distinctly yellow. Finally add acid dropwise until the well-mixed solution shows a faint change toward the pink. In order to determine the end point accurately, the beginner should have two comparison solutions both containing the same amount of indicator as used in the analysis and approximately the same volume as at the end of the titration. For one solution have the indicator in distilled water; the color will be yellow because water reacts basic to methyl orange. For the other comparison solution, add a drop of the standardized acid, or just enough to change the methyl orange color toward the pink. This shade should be matched in the titration.†

From the total volume of hydrochloric acid used, deduct the volume of hydrochloric acid corresponding to the sodium hydroxide added and this will give the volume of hydrochloric acid actually required to react with the weight of the carbonate used. The milli-equivalent weight of

* See p. 23 regarding significant figures. In general, no more significant figures should be used in analyses than corresponds to the accuracy of the result. In reporting results, the next to the last figure kept should not vary by more than 2 units.

† It is also well to have as much neutral sodium chloride present as will be formed by the titration.

Na_2CO_3 in this determination is the molecular weight divided by 2000; the same is true of Na_2O. See p. 474.

3. Determination of Alkali Carbonate and Hydroxide in the Presence of one Another

Method of C. Winkler

Of the many methods which have been proposed for this determination that of Winkler is the best.

In one portion determine the total amount of alkali present by titration with acid, using methyl orange as an indicator, and determine the hydroxide in a second portion as follows: Add the solution from a pipet to enough barium chloride solution to leave the solution about $0.1\,N$ in Ba^{++} after all the carbonate is precipitated; the following reactions take place:

$$Na_2CO_3 + BaCl_2 = 2\,NaCl + \mathbf{BaCO_3}\ \text{(insoluble)}$$
$$2\,NaOH + BaCl_2 \rightleftarrows 2\,NaCl + Ba(OH)_2\ \text{(soluble)}$$

Add phenolphthalein and titrate slowly with hydrochloric acid with constant stirring; decolorization is effected as soon as the hydroxide is neutralized before any barium carbonate is dissolved. The amount of acid used corresponds to the amount of hydroxide originally present.

4. Determination of Alkali Carbonate in the Presence of either Alkali Hydroxide or Alkali Bicarbonate

Method of R. B. Warder

If a solution of sodium hydroxide is titrated with tenth-normal hydrochloric acid, the reaction is practically complete at about $p_H = 11$. When sodium carbonate, Na_2CO_3, is titrated with tenth-normal hydrochloric acid, it is completely changed to $NaHCO_3$ at about $p_H = 10$ and the sodium bicarbonate is changed to chloride at about $p_H = 4$. It happens, fortunately, that the color change with phenolphthalein takes place after the sodium hydroxide has been completely neutralized and just after the carbonate has been converted to bicarbonate. Methyl orange, on the other hand, does not show an acid reaction until the sodium bicarbonate is changed completely to sodium chloride.

$$\left.\begin{array}{l} OH^- + H^+ \rightarrow H_2O \\ CO_3^{--} + H^+ \rightarrow HCO_3^- \end{array}\right\}\text{end point with phenolphthalein}$$
$$HCO_3^- + H^+ \rightarrow H_2O + CO_2 \uparrow\ \text{additional reaction with methyl orange}$$

In carrying out the analysis it is important to make sure that there is no loss of CO_2 before the first end point is reached; the solution must be cold, the acid must be added slowly, and each portion must be stirred in well before fresh acid is added.

Procedure. — Weigh out 5 g of the sample to four significant figures, dissolve in water, and make up to exactly 500 ml in a measuring-flask.

Mix well by pouring back and forth into a beaker at least four times, and take 25-ml portions of the solution with a pipet for the further analysis.

To one portion, add some phenolphthalein indicator, chill by placing the flask in ice-water, and titrate slowly with 0.1 N hydrochloric acid while stirring constantly. Titrate to match the rose color obtained by adding phenolphthalein indicator to a solution of approximately the same concentration of pure sodium bicarbonate. Let T_1 represent the milliliters of acid required to decolorize the solution.

To another portion add methyl orange and titrate till the color of the solution begins to change from yellow to pink. Let T_2 represent the total milliliters of acid used to make the solution acid to methyl orange.

Computation. — (*a*) If T_2 is over twice as large as T_1, the original sample is a mixture of carbonate and bicarbonate. (*b*) If T_1 is over half as large as T_2 the sample contains carbonate and hydroxide.

(*a*) Now n moles of CO_3^{--} react with n moles of H^+ in the phenolphthalein titration and with $2n$ moles of H^+ in the methyl orange titration, and m moles of HCO_3^- react with no acid in the first titration and with m moles of H^+ in the second titration. In a mixture of n moles of CO_3^{--} and m moles of HCO_3^-, using T_1 milliliters of N-normal HCl in the phenolphthalein titration and T_2 milliliters of acid in the methyl orange titration:

$$T_1 \times N = n = \text{number of milli-moles of } CO_3^{--}$$
$$(T_2 - 2\,T_1)N = m = \text{number of milli-moles of } HCO_3^-$$

(*b*) If T_2 is less than twice as large as T_1, the original sample is a mixture of alkali hydroxide and carbonate

$$(T_2 - T_1)N = \text{number of milli-moles of } CO_3^{--}$$
$$(2\,T_1 - T_2) \times N = \text{number of milli-moles of } OH^-$$

Note. — This method of analysis, which applies to the analysis of alkali carbonate, hydroxide, and bicarbonate mixtures but not to mixtures of alkaline-earth carbonate with hydroxide and bicarbonate, is not as satisfactory as Winkler's method which depends upon the titration of one sample with methyl orange as indicator and of another sample with phenolphthalein as indicator after treatment with barium chloride, which precipitates barium carbonate. A solution containing *soluble* alkali or alkaline-earth hydroxide in the presence of *insoluble* alkaline-earth carbonate, can be titrated with acid and the phenolphthalein end point obtained as soon as the hydroxide has been neutralized completely and before any of the insoluble carbonate dissolves. With methyl orange, however, the end point is not reached until all the alkaline-earth carbonate has dissolved. In this case, the carbonate dissolves very slowly toward the last; it is best, therefore, to add an excess of acid and then, when the alkaline-earth carbonate is all dissolved, titrate back to a methyl orange end point.

5. Determination of Alkaline-earth Hydroxides

Titrate with phenolphthalein as indicator to a colorless end point.

6. Determination of Alkaline-earth Carbonates

Cover the carbonate with 25 ml of water, add an excess of the standard acid, boil to remove the carbon dioxide, cool, and titrate the excess of acid with alkali, using methyl orange as indicator.

7. Determination of Alkaline-earth Oxide together with Alkaline-earth Carbonate

This analysis is based upon the fact that calcium carbonate, as well as calcium oxide, neutralizes a solution which is acid to methyl orange and changes the color of the indicator. One mole of $CaCO_3$ reacts with 2 moles HCl before the solution is acid to methyl orange. Toward phenolphthalein calcium oxide is basic, but calcium carbonate is not, and the end point is reached when all the calcium oxide is neutralized and the calcium carbonate begins to dissolve.

Suppose, for example, it is desired to determine the amount of oxide and carbonate in a sample of "quicklime." Break up the lime into pieces about the size of a pea, weigh out 14 g and slake with boiled water. Wash the paste into a 500-ml flask and dilute to the mark with water free from carbon dioxide. After thoroughly mixing, transfer 50 ml of the turbid liquid to a second 500-ml flask and again dilute to the mark.

Determination of the Total Calcium. — To 50 ml (0.14 g of substance) of the last solution add 60 ml of $0.1\,N$ hydrochloric acid and heat until there is no further evolution of carbon dioxide. Cool, and titrate the excess of acid with $0.1\,N$ sodium hydroxide solution, using methyl orange as an indicator. For this purpose t milliliters of the latter are required; consequently $60 - t$ milliliters of $0.1\,N$ acid were necessary to neutralize the calcium hydroxide and calcium carbonate in the 50 ml of the solution taken for analysis.

Determination of the Calcium Oxide. — Titrate a second portion of the freshly shaken solution with $0.1\,N$ hydrochloric acid added drop by drop to the cold solution, using phenolphthalein as an indicator. Assume that t_1 milliliters of the acid were necessary to neutralize the calcium oxide.

Consequently, for the neutralization of the $CaCO_3 + CaO$, $60 - t$ milliliters of $0.1\,N$ acid were required, and for the CaO, t_1 milliliters of $0.1\,N$ acid were necessary. For the neutralization of the $CaCO_3$, therefore, $60 - (t + t_1)$ milliliters of $0.1\,N$ acid were necessary.

50 ml solution (0.14 g lime) contain:

(*a*) $t_1 \times 0.002803$ g CaO, (*b*) $[60 - (t + t_1)] \times 0.5003$ g $CaCO_3$, and the sample contains

$$\frac{t_1 \times 0.2805}{0.14} = 2\,t_1 \text{ per cent CaO}$$

and

$$\frac{[60 - (t + t_1)] \times 0.5005}{0.14} = \text{per cent } CaCO_3$$

The above method of titration fails to take into consideration the fact that commercial lime contains more or less magnesia. As a result of coöperative analyses made by the U. S. Geological Survey, the Bureau of Chemistry, and the Bureau of Standards, using seven methods of analysis, Miss Alice I. Whitson has published the following modified Scaife method for the

8. Determination of Available Lime in Quicklime and Hydrated Lime

Weigh 1.402 g of the carefully prepared and finely ground lime (passing 100 mesh) into a 400-ml beaker, add 200 ml of hot water, cover, heat carefully, and then boil for 3 minutes.

Cool, wash down the cover glass, add 2 drops of phenolphthalein and titrate with N hydrochloric acid, adding the acid dropwise as rapidly as possible and stirring vigorously to avoid local excess of acid. When the pink color disappears in streaks, retard the rate of addition of acid somewhat, but continue until the pink color fades throughout the solution for 1–2 seconds. Note the reading and ignore the return of color.

Repeat the experiment, substituting for the 400-ml beaker a 1-l graduated flask carrying a one-hole stopper fitted with a short glass tube drawn out to a point. Cool, and add dropwise, and with vigorous stirring, about 4.5 ml less acid than before. Call this number of milliliters used A. Grind up any small lumps with a glass rod flattened at one end, dilute to the mark with freshly boiled distilled water, close the flask with a solid stopper, mix thoroughly for 4–5 minutes, and let settle for half an hour.

Pipet off a 200-ml portion, add phenolphthalein, and titrate slowly with 0.5 N hydrochloric acid until the solution remains colorless on standing one minute. Call this additional number of milliliters B. Then the percentage of available CaO = $2\,A + 5\,B$.

The computation is thus simplified because the weight of sample taken is exactly 50 times the milli-equivalent weight of calcium oxide (0.02804 g). If any other weight of sample, s, is taken and hydrochloric acid solutions of N_1 and N_2 concentrations are used instead of exactly normal and half-normal acids, the computation is as follows:

$$\frac{(A \times N_1 + 5\,B \times N_2) \times 0.02804 \times 100}{s} = \text{per}$$

9. Determination of Alkaline-earth Bicarbonates

This determination finds a practical application in the determination of the temporary hardness of water.

The hardness of a water is caused by the presence of alkaline-earth salts, either those with strong acids ($CaSO_4$, $MgCl_2$) or bicarbonates. A hard water is recognized by the fact that it gives with a clear soap solution a turbidity or even a precipitate, and considerable soap must be added before a lather is obtained on shaking. Usually calcium salts, and chiefly calcium bicarbonate, predominate in such a solution, and hardness is usually expressed in parts of calcium carbonate (or calcium oxide) in 100,000 parts of water.

If the solution contains 1 part of calcium carbonate in 100,000 parts of water it is said to possess one degree of hardness (French); if such a water contains n parts of $CaCO_3$ in the same quantity of water it possesses n degrees of hardness. In Germany the hardness is expressed in parts of CaO per 100,000 parts of water; in England the hardness is expressed in grains of calcium carbonate per Imperial gallon. In the United States hardness is usually expressed in grains of calcium carbonate per U. S. gallon, which is five-sixths as large as the Imperial gallon. One degree of hardness on the French scale = 0.56 degree on the German scale = 0.70 degree on the English scale = 0.585 degree on the U. S. scale. When magnesium salts are present, these are expressed in terms of the equivalent amounts of $CaCO_3$ or CaO. The error caused by this assumption is not great, for the amount of magnesium present is usually small compared with the amount of calcium. If a water containing calcium bicarbonate and calcium sulfate is heated to boiling, the former is decomposed with the precipitation of calcium carbonate:

$$Ca(HCO_3)_2 = H_2O + CO_2 + \mathbf{CaCO_3}$$

while the calcium sulfate remains in solution. In other words, the hardness produced by the presence of alkaline-earth bicarbonates disappears on boiling, and is designated, therefore, as "temporary hardness" to distinguish it from "permanent hardness," which is usually caused by alkaline-earth salts of the stronger acids, usually calcium sulfate. The sum of the temporary and permanent hardness of a water represents the total hardness.

According to O. Hehner, the temporary as well as permanent hardness may be determined accurately by an alkalimetric process.

(a) *Determination of Temporary Hardness*

Place 100 ml of the water to be examined in a white porcelain evaporating-dish, add a few drops of methyl orange, and titrate the solution with 0.1 N hydrochloric acid until the first change from yellow to orange takes place. From the amount of hydrochloric acid used the amount of calcium carbonate present can be calculated.

Example:

100 ml water required 2.5 ml of 0.1 N hydrochloric acid

As 1000 ml of 0.1 N hydrochloric acid neutralize $\frac{CaCO_3}{20} = 5.003$ g $CaCO_3$, 1 ml of 0.1 N hydrochloric acid will neutralize 0.005005 g $CaCO_3$ and 2.5 ml of 0.1 N hydrochloric acid corresponds to $0.005003 \times 2.5 = 0.0125$ g $CaCO_3$.

Then if 100 ml of water contain 0.0125 g $CaCO_3$, 100,000 ml of water will contain 12.5 g $CaCO_3$.

(b) *Determination of Permanent Hardness*

Treat another portion of 100 ml of the water with an excess of 0.1 N sodium carbonate solution, evaporate on the water-bath to dryness, and take up in a little freshly boiled distilled water. Filter off the residue and wash 4 times with hot water. Allow the filtrate to cool and afterwards titrate with 0.1 N hydrochloric acid, using methyl orange as indicator. If the amount of hydrochloric acid used for the titration is deducted from the total amount of sodium carbonate added to the water, the difference represents the amount of sodium carbonate required for the precipitation of the alkaline-earth salts of the strong acids.

Example. — 100 ml of water + 10 ml of 0.1 N Na_2CO_3 were evaporated to dryness, the residue extracted with water, and the filtrate titrated with 0.1 N hydrochloric acid; this required 8.7 ml of HCl. Consequently, for the precipitation of the calcium sulfate $10 - 8.7 = 1.3$ ml of 0.1 N Na_2CO_3 were necessary, which corresponds to $1.3 \times 0.005 = 0.0065$ g $CaCO_3$ per 100 ml water and 6.5 g $CaCO_3$ per 100,000 ml of water.

The permanent hardness amounts to 3.8 U. S. degrees.

Remark. — The above methods of Hehner for the determination of hardness will give reliable results only when the water contains no alkali carbonates in solution, as is usually the case with drinking-waters. For the determination of the amount of alkaline earth present in many *mineral waters* it is obvious that these methods cannot be used.

10. Determination of Alkaline-earth Salts of Strong Acids

The determination is practically the same as was indicated above. The alkaline-earth salt is precipitated by means of an excess of titrated sodium carbonate solution, and after filtration this excess is determined by titrating back with acid.

Procedure. — A solution containing calcium chloride and hydrochloric acid is to be analyzed. Place it in a measuring-flask, treat with a few drops of methyl orange and with sodium hydroxide solution until the neutral point is reached; after this add an accurately measured amount of sodium carbonate solution. Heat the solution until the precipitated calcium carbonate becomes crystalline, allow to cool, dilute to the mark, mix, filter through a dry filter, and titrate the excess of sodium carbonate titrated in an aliquot part of the filtrate. From the amount of sodium carbonate required for the precipitation of the calcium the amount of the metal can be calculated.

Remark. — Other metals which are precipitated by sodium carbonate can be determined in this way.

B. ACIDIMETRY

Acids are determined either by titration with standard alkali solution or a known amount of the latter is added and the excess titrated with standard acid. The second method requires more buret readings and is, therefore, less satisfactory than the first.

1. Determination of the Acid Contents of Dilute Mineral Acids (HCl, HNO_3, H_2SO_4)

Determine the density of the acid by means of an areometer, and from the tables in the back of this book estimate the approximate amount of acid present. Dilute a weighed amount of the acid so that the solution will have approximately the same concentration as that of the alkali to be used for the titration. Analyze by one of the following methods:

1. Place an accurately measured portion of the diluted acid (20–25 ml) in a beaker, add methyl orange, and titrate the solution with sodium hydroxide solution until a yellow color is obtained.

2. Place the dilute solution to be analyzed in a buret and titrate with it a definite volume of normal alkali hydroxide solution.

3. Titrate a definite volume of the diluted acid with 0.1 N $Ba(OH)_2$ solution or with sodium hydroxide free from carbonate, using phenolphthalein as an indicator.*

Example. — For the analysis 0.5 N NaOH was used.

The hydrochloric acid analyzed had at 15° a density of 1.122, corresponding to about 24 per cent HCl by weight.

100 ml 0.5 N sodium hydroxide are equivalent to 1.823 g of HCl, and conse-

* When phenolphthalein is used as an indicator in cold solutions the acids must be diluted with water free from carbonate.

quently $\frac{1.823}{0.24} = 7.595$ g of the above acid would be required to make 100 ml of 0.5 N acid, if it contained exactly 24 per cent HCl. Weigh out about this quantity (say 8 g), and as the density of the solution is 1.122, this will require $\frac{8}{1.122} = 7$ ml. Place 7 ml of the acid in a tared, glass-stoppered weighing-tube, weigh the tube and its contents, rinse the latter into a 100-ml measuring-flask and dilute with distilled water up to the mark. After thoroughly mixing, measure off 25 ml of the acid and analyze by one of the above methods. If in an analysis the original weight of the acid amounted to 7.962 g and 25 ml of the diluted acid required 25.80 ml of 0.5 N alkali, then 100 ml would require $25.80 \times 4 = 103.2$ ml of 0.5 N alkali, corresponding to $103.2 \times 0.01823 = 1.881$ g HCl. The acid, therefore, contains $\frac{1.881 \times 100}{7.962} =$ 23.6 per cent HCl.

Remark. — Instead of weighing out the acid for the analysis, it can be measured and from the percentage by volume found the percentage by weight calculated. However, as the density as determined by an areometer is not very accurate, it is better to weigh the acid. If the density of the acid is taken with a pycnometer, using all necessary precautions (cf. Kohlrausch, *Leitfaden der praktischen Physik*), it is a matter of indifference whether the acid used for the analysis is weighed or measured.

2. Analysis of Commercial Hydrous Stannic Chloride

Stannic chloride, as used for a mordant in dyeing, is obtained as the solid salt $SnCl_4 + 5\,H_2O$, or in a concentrated aqueous solution of about 50° Bé. (*d.* 1.52). The solution is obtained by dissolving metallic tin in hydrochloric acid and oxidizing the stannous chloride formed either with potassium chlorate or potassium nitrate. The preparation should contain no free acid, especially nitric acid, no stannous chloride, and no iron. The substance is, therefore, tested qualitatively for these substances as follows:

For *stannous* chloride, by dissolving in water (or diluting the concentrated solution) and adding mercuric chloride; a white precipitate of mercurous chloride shows the presence of bivalent tin.

For *nitric acid*, by means of ferrous sulfate and concentrated sulfuric acid.

For *sulfuric acid* (caused by the use of impure hydrochloric acid in the preparation of the salt) with barium chloride.

For *iron*, with potassium thiocyanate.

The solid salt $SnCl_4 + 5\,H_2O$, made by treating anhydrous stannic chloride with the calculated amount of water, is usually very pure.

The gravimetric determination of both the tin and the chlorine has been described on p. 300, but here will be given a method for determining the amount of the chlorine volumetrically.

If stannic chloride is diluted with water, the salt undergoes hydrolysis

and the solution reacts acid:

$$SnCl_4 + 4\,HOH \rightleftarrows Sn(OH)_4 + 4\,HCl$$

Consequently if methyl orange is added to the diluted solution, the acid content can be titrated with sodium hydroxide solution, and from the amount used the chlorine combined with the tin can be calculated, provided no other acid is present. If the stannic chloride was prepared by oxidation with potassium chlorate or nitrate,* the solution will also contain chlorine combined with potassium. The total chlorine can be determined by adding a few drops of neutral potassium chromate solution to the solution which has been titrated with sodium hydroxide and titrating with silver nitrate solution. If in this way more chlorine is found than corresponds to the amount of hydrochloric acid neutralized by the alkali, the difference is expressed in terms of potassium chloride. If, on the other hand, less chlorine is found, the presence of some other acid in the tin solution is assured.

To illustrate the accuracy of such an analysis, the following results will be given: A sample of solid stannic chloride ($SnCl_4 + 5\,H_2O$) was analyzed gravimetrically, as described on p. 300. It was found to contain 42.02 per cent of chlorine and 34.73 per cent of tin.

Two portions were then analyzed volumetrically by titration first with sodium hydroxide and then with silver nitrate:

A. 0.8533 g of tin salt required 20.06 ml of 0.5 *N* sodium hydroxide and 20.34 ml of 0.5 *N* silver nitrate. The total chloride content was therefore

$$0.03546 \times 0.5 \times \frac{20.35 \times 100}{0.8533} = 42.25 \text{ p}$$

The chloride present as $SnCl_4$ was

$$\frac{0.03546 \times 0.5 \times 20.06 \times 100}{0.8533} = 41.76 \text{ per cent}$$

B. 0.8383 g of tin salt required 19.79 ml of 0.5 *N* sodium hydroxide and 19.92 ml of 0.5 *N* silver nitrate. This corresponds to 42.12 per cent of total chlorine and 41.84 per cent of chlorine as stannic salt.

The above analysis shows that the tin salt was practically free from potassium chloride by the comparative agreement of the results obtained by titration with sodium hydroxide with those of the silver nitrate titration. In the absence of excess hydrochloric acid, the tin can be

* The potassium nitrate is acted upon by the excess of hydrochloric acid present forming the chloride, and the excess of the acid is afterwards removed by evaporation as much as possible.

determined from the amount of chlorine found:

$$\frac{19.79 \times 0.5 \times 0.02968 \times 100}{0.8383} = 35.13 \text{ pe}$$

instead of 34.73 per cent as found gravimetrically.

3. Determination of the Acid Content of Fuming Acids

Highly concentrated acids must be always weighed and not measured volumetrically, in order to avoid loss by evaporation. The weighing is best accomplished by means of the Lunge-Rey pipet, shown in Fig. 110.

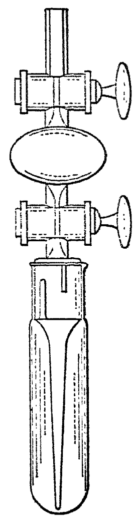


Fig. 110.

Remove the lower tube, introduce 0.5 ml of water, and weigh together with the dry upper pipet, but leaving the 2 parts unconnected. Close the lower stopcock, open the upper one, and produce a slight vacuum in the bulb by sucking through the upper tube and then closing the stopcock. Dip the dry point of the pipet into the fuming acid (in the case of solid pyrosulfuric acid, first melt it by warming slightly), and open the lower stopcock. As soon as the widened part of the pipet below the lower bulb is one-half to three-fourths full, close the stopcock, taking care that none of the liquid reaches up to it.

Carefully wipe off the acid on the outside of the pipet with filter paper; connect the two parts of the pipet and again weigh. The quantity of acid taken for the analysis should amount to 0.5–1 g. Dip the point of the pipet into about 100 ml of distilled water contained in a beaker, and, by opening first the upper stopcock and then the lower, allow the acid to run into the water. Rinse out the pipet and add the rinsings to the contents of beaker.

If the acid to be analyzed is hydrochloric or sulfuric acid, add methyl orange and titrate the solution with a 0.5 N sodium hydroxide. If it is nitric acid, first add an excess of sodium hydroxide, then a little methyl orange, and then titrate with 0.5 N hydrochloric acid. In this way the action of the ever-present nitrous acid upon the indicator is avoided. When one of the above pipets is not available, the weighing out of the sample for analysis can be effected as follows: Make a thin-walled bulb with about 1-ml capacity between two ends of capillary tubing. After weighing, connect the upper piece of capillary tubing with a small, ordinary pipet at the ends of which are attached pieces of rubber tubing, closed with pinchcocks. Fill the bulb as follows:

Close the lower pinchcock, open the upper one, and produce a vacuum by sucking through the upper tube and then closing the pinchcock. Dip the lower point of the weighed tube into the acid and open the lower pinchcock. When the small bulb is one-third full, close the pinchcock, melt the upper end of the capillary tubing, and, after wiping off the acid from the outside, likewise seal the lower end and weigh the bulb. Place 100 ml of water in a flask with a closely fitting ground-glass stopper, drop in the weighed bulb, and break it by shaking. In this way the very strongest, fuming sulfuric acid can be dissolved in water without loss. On the other hand, the pipet shown in Fig. 110 is not so good for the weighing out of an acid containing 70 per cent or more of SO_3. If the acid is not too concentrated, this bulb may be emptied as was described for the pipet.

For the analysis of the solid anhydride, Stroof places a little in a dry weighing tube, and adds concentrated sulfuric acid of known strength until a fuming acid of about 70 per cent SO_3 is obtained. To effect solution, the mixture is warmed to about 30°–40° in a loosely stoppered bottle. The acid thus obtained is analyzed as above.*

Computation. — Fuming sulfuric acid can be considered to be a solution of anhydrous SO_3 in H_2SO_4.† On treatment with water, the following reaction takes place: $SO_3 + H_2O = H_2SO_4$. The titration with NaOH, therefore, shows the total acid present, including that formed from the anhydride. Let p be the weight of the original sample and n the milliliter of N-normal NaOH used. The total weight of H_2SO_4 (equivalent weight 49) in the solution after the reaction with water is

$$n \times N \times 0.049 = p_2$$

Then $p_2 - p$ is the weight of the water which reacted with the anhydrous SO_3. Since 1 mole of H_2O (18.02 g) reacts with 1 mole of SO_3 (80.06 g), evidently 1 g of H_2O reacts with $\frac{80.06}{18.02} = 4.443$ g of SO_3 and $p_2 - p$ grams of water are equivalent to $4.443(p_2 - p)$ grams of anhydrous SO_3. This value subtracted from the weight, p, gives the original weight of H_2SO_4.

A similar computation applies to the analysis of a mixture of acetic acid and acetic anhydride. When treated with water the latter reacts as follows: $(CH_3CO)_2O + H_2O = 2\ CH_3CO_2H$ (acetic acid). The result of the NaOH titration, expressed in terms of acetic acid, will give a weight larger than that of the original sample, the excess representing the weight of water that reacted with the anhydride; and the chemical factor for converting this weight of water into the equivalent weight of the anhydride is

$$\frac{(CH_3CO)_2O}{H_2O} = \frac{72.05}{18.02}$$

* G. Finch (*Chem. Ztg.*, **1910**, 297) and R. H. Vernon (*ibid.*, **1910**, 702) use a different apparatus and larger samples, thus getting more accurate results.

† Fuming sulfuric acid contains a little SO_2 but as its determination involves an iodometric titration it will not be considered here.

Preparation of Concentrated Sulfuric Acid Mixtures (M. Gerster)

It is often necessary to prepare fuming sulfuric acid of definite concentration.

Given:

(*a*) Fuming sulfuric acid (A) with a per cent free SO_3.
(*b*) Sulfuric acid (B) with c per cent H_2SO_4 and $100 - c$ per cent water.

A fuming acid containing b per cent free SO_3 is desired.

To obtain the latter, mix 100 g of the acid A with x grams of the acid B.

The final mixture $(100 + x)g$ will contain $\frac{(100 + x)b}{100}$ grams of free SO_3. The original free SO_3 in A will react partly with the water in the acid B to form H_2SO_4. Therefore, since 1 g of H_2O reacts with 4.44 g of SO_3 and since all the water $\left(\frac{x(100 - c)}{100} \text{ grams}\right)$ must be converted to H_2SO_4, we have

$$\frac{(100 + x)b}{100} = a - \frac{4.44\,(x)(100 - c)}{100}$$

and

$$x = \frac{100\,(a - b)}{444 + b - 4.44\,c} \text{ grams of } B$$

Example. — How much acid containing 98.2 per cent H_2SO_4 should be mixed with 100 g of oleum containing 25.5 per cent free SO_3 to give an acid with 19.0 per cent free SO_3? *Ans.* 24.07 g.

5. Titration of Hydroxylamine Salts

Hydroxylamine hydrochloride reacts neutral towards methyl orange and acid towards phenolphthalein. If phenolphthalein is added to an aqueous solution of the salt, and the titration is made with 0.1 N alkali, the end point will be obtained when the total amount of acid present has been neutralized by the alkali. It is impossible to determine the amount of free hydrochloric acid present when phenolphthalein is used, but it can be done with methyl orange. Romijn* recommends for the titration of the acid a 0.1 N borax solution.

6. Hydrofluoric Acid

1000 ml normal alkali = HF = 20.01 g HF

Hydrofluoric acid can be titrated with phenolphthalein as an indicator, but not with litmus or methyl orange. Measure out the acid

* *Z. anal. Chem.*, **36**, 19 (1897). This method has not been tested in the author's laboratory.

into a platinum dish by means of a pipet which is coated with beeswax, add an excess of sodium hydroxide free from carbonate and titrate the excess of the latter in hot solution with an acid of known strength.*

A neutral fluoride can be titrated with fair accuracy by adding neutral ferrichloride solution until an end point is obtained with KCNS†

$$6\,NaF + FeCl_3 = Na_3FeF_6 + 3\,NaCl$$

Considerable sodium chloride should be added to precipitate the complex salt.

7. Fluosilicic Acid

The titration of this acid may take place according to either of the following reactions:

$$\text{I. } H_2SiF_6 + 2\,KOH = K_2SiF_6 + 2\,H_2O$$

$$\text{II. } H_2SiF_6 + 6\,KOH = 6\,KF + 2\,H_2O + Si(OH)_4$$

According to Equation I

1000 ml normal KOH or $Ba(OH)_2$ = 72.04 g H_2SiF_6

Treadwell's Method

If fluosilicic acid is titrated in the cold with caustic potash, using phenolphthalein as indicator, a red color appears after a time, but disappears later on account of the excess alkali reacting with K_2SiF_6 to form 6 KF and $Si(OH)_4$.

This last reaction, however, takes place so slowly that it is impossible to obtain a distinct end point. If the solution is diluted with an equal volume of alcohol, however, then 2 or 3 drops of phenolphthalein added, the secondary reaction is prevented and the acid can be titrated with tenth-normal potassium or barium hydroxide. The insoluble potassium or barium fluosilicate separates out and is not acted upon by an excess of the alkali, so that a sharp end point is obtained as soon as all of the H_2SiF_6 has been changed to K_2SiF_6. Sodium hydroxide forms a soluble salt so that the titration cannot be made with this reagent.

Indirect Method of Penfield‡

Penfield treats the solution to be titrated with an excess of KCl, dilutes with an equal volume of alcohol, and then titrates the hydrochloric acid set free in the reaction

$$H_2SiF_6 + 2\,KCl = K_2SiF_6 + 2\,HCl$$

* Cf. Winteler, *Z. angew. Chem.*, **1902**, 33.

† Greeff, *Ber.*, **36**, 2511 (1913).

‡ *Chem. News*, **39**, 179.

with tenth-normal sodium hydroxide solution, using cochineal as indicator. Methyl red is preferable to the cochineal.

According to Equation II

1000 ml normal $NaOH = 24.01$ g H_2SiF_6

*(a) Method of Sahlbom and Hinrichsen**

Titrate the solution at the temperature of the water-bath with tenth-normal sodium hydroxide solution, using phenolphthalein as indicator.

(b) Method of Schucht and Möller†

Treat the solution to be titrated with an excess of neutral calcium chloride solution (25 ml of $4N$ $CaCl_2$) and titrate with tenth-normal sodium hydroxide, using methyl orange as indicator. The following reaction takes place in the cold:

$$H_2SiF_6 + 3\,CaCl_2 + 6\,NaOH = 3\,CaF_2 + 6\,NaCl + Si(OH)_4 + 2\,H_2O$$

During the titration the solution remains clear, for the CaF_2 and the $Si(OH)_4$ remain in colloidal solution. Phenolphthalein should not be used as indicator, as it is hard to decide upon the correct end point.

In the titration of salts of fluosilicic acid, however, the titration must always be carried out with phenolphthalein as indicator:

$$Na_2SiF_6 + 3\,CaCl_2 + 4\,NaOH = 3\,CaF_2 + 6\,NaCl + Si(OH)_4$$

In this case

$$1000 \text{ ml of normal } NaOH = 47.01 \text{ g of } Na_2SiF_6$$

8. Determination of Organic Acids

Methyl orange cannot be used for the titration of organic acids, but either phenolphthalein or litmus may be employed. If carbonic acid is present at the same time, the titration can be made in a hot solution (cf. p. 505). It is best to dilute the organic acid with water free from carbon dioxide, add phenolphthalein, and titrate with half-normal barium hydroxide in the cold.

To illustrate. — It is desired to analyze a sample of acetic anhydride. The only impurity that the distilled product is likely to contain is acetic acid, so that it is a question of determining the amount of acid and anhydride in the presence of one another. Such a problem can be solved only by an indirect analysis. Weigh out the mixture in a small glass bulb and drop it into an accurately measured volume of standard

* *Ber.*, **39**, 2609 (1906).

† *Ber.*, **39**, 3693 (1906).

barium hydroxide solution contained in a flask which is connected with a return-flow condenser and a soda-lime tube at the top. Heat gently until the anhydride has dissolved completely; it is thereby changed to acetic acid

$$\begin{matrix} CH_3CO \\ \end{matrix}\!\!\!>\!O + H_2O = 2\,CH_3COOH$$

which is neutralized by the base. After the reaction is complete, add a drop of phenolphthalein and titrate the excess of barium hydroxide with $0.1\,N$ acid. Let x = weight of acetic anhydride and y the weight of acetic acid originally present. Then

$$x + y = p \text{ (original weight)}$$
$$mx + y = q \text{ (weight acetic acid after the action of water)}$$

and
$$x = \frac{1}{m-1}(q-p)$$

In these equations $m = \dfrac{2\,C_2H_4O_2}{C_4H_6O_3} = \dfrac{120.06}{102.05} = 1.176$

and
$$\frac{1}{m-1} = 5.66$$

Example. — A sample of acetic anhydride was analyzed in this way: Weight of sample, 0.9665 g. Used 200 ml of $Ba(OH)_2$ solution which was equivalent to 187.8 ml of 0.1 N acid. After the reaction, 6.03 ml of 0.1 N HCl were used. Find percentage of acetic acid and of acetic acid in the commercial preparation.

Ans. 73.04 per cent acetic anhydride and 26.96 per cent of acetic acid.

Remark. — Acetic acid anhydride is also hydrolyzed by water at the ordinary temperature. If a weighed amount of the substance is shaken with water in a flask until no more drops of anhydride are to be recognized and the acetic acid formed is then titrated with barium hydroxide, using phenolphthalein as indicator, correct results are obtained if the water used is entirely free from carbon dioxide. It is always safer, however, to carry out the determination as outlined above.

In some factories the analysis of acetic acid anhydride is carried out by the method of Menschutkin and Wasiljeff. This is based upon the fact that when acetic acid anhydride is treated with freshly distilled aniline, acetanilide is formed in accordance with the following equation:

$$\begin{matrix} CH_3\cdot CO \\ CH_3\cdot CO \end{matrix}\!\!>\!O + C_6H_5NH_2 = C_6H_5N(C_2H_3O)H + CH_3COOH$$

whereas acetic acid itself does not form acetanilide under the same conditions. Two or three grams of commercial acetic anhydride are shaken in a dry weighing beaker with 4–6 ml of freshly distilled aniline. The anhydride immediately begins to combine with the aniline, liberating considerable heat. After cooling, the solidified contents of the weighing beaker are rinsed by means of absolute alcohol into an ordinary beaker, phenolphthalein is added and the total amount of acetic acid present titrated with half-normal alkali.

We have then, using the same notation as before,

$$C_4H_6O_3 \quad = p$$

$$mx + \quad = q \text{ (acetic acid)}$$

from which can be computed

$$x = \frac{p - q}{1 - m}$$

In this equation

$$\frac{C_2H_4O_2}{C_4H_6O_3} = \frac{60.03}{102.05} = 0.5880$$

and

$$\frac{1}{1 - m} = 2.428$$

It is true that concordant results are obtained by this method, but they are much too high; indeed, as much as 14–16 per cent too high. This is due to the fact that although acetic acid itself does not react with aniline in the cold, it does react very readily when heated. When, therefore, a mixture of acetic anhydride and acetic acid is allowed to remain in contact with aniline, so much heat is liberated from the reaction between the anhydride and the aniline that a part of the acetic acid itself reacts and takes part in the formation of acetanilide:

$$CH_3CO_2H + C_6H_5NH_2 = H_2O + C_6$$

so that evidently too little acetic acid is found in the subsequent titration and consequently too high values are obtained for the amount of anhydride present.

9. Determination of Sulfurous Acid

For the determination of sulfurous acid by itself, the analysis is best accomplished, as recommended by Volhard, by an iodometric process, *i.e.*, it is oxidized to sulfuric acid. In many cases, however, it is necessary to titrate the sulfurous acid with alkali hydroxide (cf. p. 488). Methyl orange should be used as indicator and only one hydrogen in the H_2SO_3 is titrated:

Titration with phenolphthalein gives approximately complete neutralization but the results are reliable only when an excess of neutral hydrogen peroxide is added which oxidizes the sulfurous acid.

10. Determination of Thiosulfuric Acid*

To a large excess of mercuric chloride (20 ml of the cold, saturated solution for each millimole of $Na_2S_2O_3$) add a measured volume of sodium thiosulfate solution. Shake several times and allow to stand 5 minutes. Then to prevent precipitation of HgO, add 30 ml of 4 N ammonium chloride solution, and titrate with 0.1 N sodium hydroxide

* W. Feld, *Z. angew. Chem.*, **24**, 290, 1161 (1911); A. Sander, *ibid.*, **1915**, 9; **1916**, 16.

using methyl orange as indicator:

$$(a)\ 2\,Na_2S_2O_3 + 2\,HgCl_2 = 2\,HgS_2O_3 + 4\,NaCl$$
$$(b)\ 2\,HgS_2O_3 + 2\,H_2O = 2\,HgS + 2\,H_2SO_4$$
$$(c)\ 2\,HgS + HgCl_2 = Hg_3S_2Cl_2$$

If too little $HgCl_2$ is present, black mercuric sulfide precipitates and makes the titration difficult.

Polythionates can be titrated similarly,* as the following equations show:

$$2\,K_2S_3O_6 + 3\,HgCl_2 + 4\,H_2O = Hg_3S_2Cl_2 + 4\,KCl + 4\,H_2SO_4$$
$$2\,K_2S_4O_6 + 3\,HgCl_2 + 4\,H_2O = Hg_3S_2Cl_2 + 2\,S + 4\,KCl + 4\,H_2SO_4$$

According to Eliasberg,† the thiosulfates and polythionates can be determined by treatment with a measured quantity of alkali hydroxide solution and neutral hydrogen peroxide, boiling to complete the oxidation, and titrating the excess of base with $0.1\,N$ acid.

$$Na_2S_2O_3 + 4\,H_2O_2 + H_2O = Na_2SO_4 + 4\,H_2O + H_2SO_4$$
$$Na_2S_4O_6 + 7\,H_2O_2 + 2\,H_2O = Na_2SO_4 + 6\,H_2O + 3\,H_2SO_4$$

11. Determination of Orthophosphoric Acid

NaH_2PO_4 reacts acid toward phenolphthalein, and neutral toward methyl orange; Na_2HPO_4 is neutral toward the former indicator and basic toward the latter.

Therefore, on titrating free phosphoric acid with alkali one of the following reactions will take place:

1. $H_3PO_4 + 2\,NaOH = Na_2HPO_4 + 2\,H_2O$ (phenolphthalein)
2. $H_3PO_4 + NaOH = NaH_2PO_4 + H_2O$ (methyl orange)

The first reaction is not altogether sharp, because pure Na_2HPO_4 is dissociated to a slight extent, so that it becomes alkaline to phenolphthalein:

$$Na_2HPO_4 + HOH \rightleftarrows NaH_2PO_4 + NaOH$$

To prevent this hydrolysis, the titration is best effected in a cold, concentrated solution containing sodium chloride.

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* Kessler, *J. prakt. Chem.*, **47**, 42 (1849).

† *Ber.*, **19**, 322 (1866).

12. Alkalimetric Determination of Phosphorus in Iron and Steel*

1000 ml normal NaOH = 1.349 g P

Procedure. — Weigh 2 g of steel to the nearest centigram into a 250-ml Erlenmeyer flask, add 100 ml of 4 *N* nitric acid, and insert a small, short-stemmed funnel into the neck of the flask. Heat until the sample is all dissolved and very little oxide of nitrogen is visible in the neck of the flask. Add 10 ml of 1.5 per cent $KMnO_4$ solution and boil for 2 to 3 minutes. The purpose of the permanganate is to oxidize the dissolved carbide and to make sure that all the phosphorus is fully oxidized to phosphoric acid. If no precipitate appears, add more permanganate and boil again. Dissolve the precipitate by adding a few drops of sulfurous acid, a small crystal of ferrous sulfate, or some 5 per cent sodium thiosulfate solution. Add very little of the reducing agent at a time, but continue adding it, at short intervals, until the manganese dioxide is dissolved. If there is any appreciable silicious residue at this point it should be removed by filtration. Boil 2 minutes after the manganese dioxide has dissolved and then cool to 40°. If the volume of the solution is less than about 80 ml at this stage of the analysis, more 4 *N* nitric acid should be added. Add 40 ml of 6 *N* ammonium hydroxide in portions of 25, 10, and 5 ml, and rotate the flask until the precipitated ferric hydroxide redissolves. It is important that the solution should now assume a pale straw color and not appear at all red from colloidal ferric hydroxide. A red solution shows that too much ammonia was added and the precipitation of the phosphorus will be incomplete. With the solution at 35–40° add 40 ml of ammonium molybdate solution.† Stopper the flask with a rubber stopper and shake vigorously for 5 minutes; allow the precipitate to settle for 15 minutes but in no case over half an hour.

Filter off the precipitate and use a 9-cm washed filter paper that fits the funnel tightly. Wash the flask, precipitate, and paper twice with 5-ml portions of 1 per cent HNO_3 (1 ml concentrated acid to 100 ml of water) and then 5 times with 5-ml portions of 1 per cent KNO_3 solution. Finally wash the paper with cold, 1 per cent KNO_3 until 10 ml of the last filtrate will not decolorize 1 drop (0.03 ml) of 0.1 *N* NaOH and 1 drop of phenolphthalein indicator solution. This usually requires about

* The method was proposed by Hundeshagen and also by Manby but was modified by J. O. Handy. The above directions were obtained from the Bureau of Standards.

† Stir 100 g of pure MoO_3 into 400 ml of cold distilled water and add 80 ml of concentrated ammonium hydroxide. Filter and pour while stirring into 1 l of 6 *N* nitric acid. Add 50 mg of microcosmic salt, and allow to stand 24 hours before using. Do not prepare more than a week's supply of the acid reagent at a time.

10 washings more than are specified above. Direct the dilute KNO_3 solution around the edge of the filter and then spirally down, and wait until the liquid has drained before washing again.

Return the paper and the precipitate to the Erlenmeyer flask in which the precipitation took place, add 25 ml of water, 3 drops of phenolphthalein indicator solution, and, from a buret or pipet, 10 ml of $0.1\,N$ NaOH free from carbonate. This will be sufficient in most cases to dissolve all the yellow precipitate and leave the solution alkaline to phenolphthalein. If necessary add more NaOH. Discharge the pink color by adding a measured volume of $0.1\,N$ HNO_3 from a buret, and finish the titration by adding just enough more of the $0.1\,N$ NaOH to impart a pink color to the solution.

The chemical equation that represents the dissolving of the precipitate, with the solution left neutral to phenolphthalein (cf. p. 528), is the following

$$(NH_4)_3PO_4{\cdot}12MoO_3 + 23\,OH^- \rightarrow 12\,MoO_4^{--} + 3\,NH_4^+ + HPO_4^{--} + 11\,H_2O$$

From this equation it is clear that

$$1\,P \approx 12\,Mo \approx 23\,OH^-$$

... of analysis is $\frac{\quad}{23{,}000}$ = 0.001349 g of phosphorus.

Modified Procedure of C. M. Johnson*

Partly because an acid solution of molybdate is not very stable and is useful only when relatively fresh, and partly because of difficulty in the analysis of alloy steels to get accurate results in the presence of vanadium, Johnson prefers to use a neutral solution of ammonium molybdate (cf. p. 531) which keeps indefinitely.

Solutions Required

Standard Sodium Hydroxide and Standard Nitric Acid. — If many analyses are to be made, it is convenient to have these solutions of equal concentration, approximately $0.125\,N$. Since 1 ml of normal sodium hydroxide is equivalent to 0.001349 g of phosphorus, if a sample of steel is taken of which the weight in grams is 13.49 times the normality of the sodium hydroxide (and nitric acid), the percentage of phosphorus in the steel can be determined by subtracting the volume of nitric acid (in millimeters) from the total volume of sodium hydroxide used and moving the decimal point two places to the left.

Dissolve 21 g of pure sodium hydroxide and 0.1 g of barium hydroxide in 2 l of water. Stir the solution well, allow it to stand over

* *J. Ind. Eng. Chem.*, **11**, 113 (1919).

night, and filter, or decant off the clear solution. Dilute the solution with 2 l more of water and mix thoroughly.

Dilute 83 ml of 6 N nitric acid (d. 1.2) with distilled water to a volume of 4 l and shake well.

Titrate the two solutions against one another and dilute the stronger solution until both solutions are equivalent. Standardize the alkali against pure potassium acid phthalate (cf. p. 500), using phenolphthalein as indicator.

The standardization of the alkali should take place in the cold, exactly as in the analysis of the precipitate. A slight error is introduced by the action of carbonic acid in the air, but in determining the phosphorus in steel the result is never good to more than 3 significant figures, so that this error is not serious. The barium hydroxide is added to precipitate any carbonate in the caustic soda. The sodium hydroxide solution should be protected from carbonic acid as much as possible by keeping it in a bottle as described on p. 506.

Ferrous Sulfate Solution. — Dissolve 25 g of ferrous sulfate or 40 g of ferrous ammonium sulfate in 180 ml of concentrated sulfuric acid and 820 ml of water.

Strong Permanganate. — Dissolve 25 g of potassium permanganate in 1 l of water.

Nitrate Wash. — Use 1 g of potassium nitrate per liter.

Acid Wash. — Dilute 32 ml of 6 N nitric acid to 1 l.

Ammonium Molybdate. — Place 55 g of ammonium molybdate and 50 g of ammonium nitrate in a liter beaker, add 45 ml of 6 N ammonia, and dilute to 700 ml. Heat with occasional stirring until nearly all the solid has dissolved. After standing over night decant off the clear solution through a double filter but do not wash the residue.

Procedure. — Weigh out to the nearest centigram about 1.68 g of steel and dissolve in 45 ml of 4 N nitric acid, heating over a low flame with the beaker covered. If much carbonaceous residue remains, filter and wash the residue 6 times with the acid wash.

Add about 3 ml of the permanganate and boil 3 minutes to complete the oxidation of the phosphorus and dissolved carbides. Then add just enough of the ferrous sulfate solution to dissolve the precipitated manganese dioxide (3 ml should be sufficient). Boil out the nitrous fumes and add 15 ml of 16 N nitric acid. Rinse off the cover glass and sides of the beaker with a little hot water, and add to the hot solution 50 ml of ammonium molybdate solution. Stir vigorously for 2 minutes, and allow the precipitate to settle for 20 minutes or a little longer. Filter; wash the precipitate 12 times with small portions of the nitric acid wash and then with the potassium nitrate wash till all acid is

removed. This may require 40 washings with a high-phosphorus steel. The washing should be done promptly without allowing the precipitate to remain dry for any length of time. The outside fold of the filter should have no sour taste when the washing is finished.

Place the filter and precipitate in a 150-ml beaker, and add from a buret enough standard sodium hydroxide solution to cause the yellow color of the precipitate to disappear on macerating the filter to a pulp with a rubber-tipped stirring-rod. Dilute the solution to about 30 ml, add a drop of phenolphthalein, and titrate carefully with nitric acid until the pink color disappears.

13. Determination of Boric Acid

Free boric acid has no action upon methyl orange, consequently alkali borates may be titrated with hydrochloric and nitric acids, using this indicator; with sulfuric acid the results are not as satisfactory, for there is in this case no sharp color change. If phenolphthalein is used as the indicator, the red color fades gradually and the end point cannot be determined with certainty. If, on the other hand, sodium hydroxide is slowly run into an aqueous solution of boric acid containing phenolphthalein, after some time a pale pink color is noticeable which becomes deeper on the addition of more alkali. The first pink color is formed before all the boric acid has been neutralized, for sodium borate is perceptibly hydrolyzed. Free boric acid cannot be titrated by itself, but if, as proposed by Jörgensen,* a sufficient amount of glycerol† (or mannitol‡) is added to the solution, the hydrolysis is prevented, so that when 1 mole of NaOH is present for 1 mole of H_3BO_3 the solution suddenly changes from colorless to red; probably a stronger acid is formed by the addition of the glycerol, the glycerylboric acid $(C_3H_5O_2OH)B(OH)$.

If the solution does not contain sufficient glycerol the color change takes place too soon, as can be shown by the addition of more glycerol. If the red color disappears on adding the glycerol, more alkali is added until it reappears. The right end point is reached when the red color no longer disappears on the addition of glycerol. Inasmuch as commercial glycerol reacts acid, it must be just neutralized with alkali before being used for this determination. Furthermore, in order to obtain accurate results it is necessary that the solutions should be absolutely free from carbonate.

* *Z. Nahrungsm.* **9**, 389, and *Z. angew. Chem.*, **1897**, 5.

† *Z. angew. Chem.*, **1896**, 549.

‡ Jones, *Am. J. Sci.* [4], **7**, 147 (1899).

*Application. Determination of Boric Acid in an Alkali Borate Free from Carbonate**

Dissolve about 30 g of the borate in water free from carbon dioxide, dilute to 1 l, and determine the total alkali in an aliquot part by titration with 0.5 *N* hydrochloric acid, using methyl orange as an indicator. Take another aliquot part of the borate solution and exactly neutralize by the amount of hydrochloric acid found necessary by the previous titration; by this means the solution will contain free boric acid. After adding about 50 ml of glycerol for each 1.5 g of the borate, titrate the solution with 0.1 *N* sodium hydroxide, using phenolphthalein as indicator. When the end point is reached, add 10 ml more of glycerol, and this usually causes the solution to become colorless. Again add sodium hydroxide and repeat the process until finally the addition of glycerol causes no further action upon the end point.

If the borate contained carbonate, neutralize the portion taken for analysis with acid as before, then boil for a few minutes, taking the precaution of connecting the flask containing the solution with a return-flow condenser.† After the carbon dioxide is expelled, wash down the sides of the condenser with water and titrate with sodium hydroxide.‡

For the determination of boric acid in the presence of mineral acid,§ add an excess of potassium iodide and iodate. The mineral acid reacts with the iodide-iodate mixture and sets free iodine (cf. p. 96), but boric acid does not do this. Discharge the iodine color with dilute sodium thiosulfate, added dropwise and avoiding an excess. Then add 1–2 g of mannitol and titrate with 0.1 *N* sodium hydroxide, using phenolphthalein as indicator.

If considerable mineral acid is present, neutralize the most of it with caustic alkali solution before adding the iodate-iodide mixture.

Determination of Boric Acid in Insoluble Silicates

See E. T. Wherry and W. H. Chapin, *J. Am. Chem. Soc.*, **30**, 1687 (1908).

14. Determination of Carbonic Acid

(*a*) *Determination of Free Carbonic Acid*

To determine the amount of free carbonic acid present in a dilute aqueous solution, add an excess of 0.1 *N* barium hydroxide solution,

* M. Hönig and G. Spitz, *Z. angew. Chem.*, **1896**, 549.

† The condenser serves to keep back any boric acid escaping with the steam.

‡ Instead of the glycerol, about 1 g of mannitol can be used to advantage.

§ Jones, *loc. cit.*

and determine the excess with 0.1 *N* HCl, using phenolphthalein as an indicator:

$$H_2CO_3 + Ba(OH)_2 = BaCO_3 + 2\,H_2O$$
$$1 \text{ ml of } 0.1\,N \text{ HCl} = 0.0022 \text{ g } CO_2$$

(*b*) *Determination of Carbon Dioxide Present as Bicarbonate*

Titrate the solution with 0.1 *N* HCl in the presence of methyl orange:

$$NaHCO_3 + HCl = NaCl + H_2CO_3$$
$$1 \text{ ml of } 0.1\,N \text{ HCl} = 0.0044 \text{ g } CO_2$$

(*c*) *Determination of Carbon Dioxide Present as Carbonate*

Titrate with 0.1 *N* HCl and methyl orange:

$$Na_2CO_3 + 2\,HCl = 2\,NaCl + H_2CO_3$$
$$1 \text{ ml of } 0.1\,N \text{ HCl} = 0.0022 \text{ g } CO_2$$

Dissolve an alkaline-earth carbonate in an excess of 0.1 *N* acid and titrate back with 0.1 *N* acid.

(*d*) *Determination of Free Carbonic Acid in the Presence of Bicarbonate*

Titrate one portion with 0.1 *N* HCl, using methyl orange as indicator, and determine the amount of bicarbonate as under (*b*).

Treat a second portion with an excess of barium chloride* then with an excess of barium hydroxide, and titrate the excess of the hydroxide with HCl, using phenolphthalein as indicator. If the volume of 0.1 *N* acid used for the first titration is deducted from the volume of 0.1 *N* barium hydroxide solution found to be necessary in the last titration, the difference multiplied by 0.0022 will give the amount of free carbonic acid.†

(*e*) *Determination of Alkali Bicarbonate in the Presence of Carbonate*

See p. 512.

15. Determination of Carbonic Acid in the Air. Method of Pettenkofer

Principle. — A large, measured volume of air is treated with an excess of titrated barium hydroxide solution whereby the carbon dioxide is quantitatively absorbed, forming insoluble barium carbonate. Phenolphthalein is added, and the excess of barium hydroxide is determined by titration with hydrochloric acid until the solu-

* The addition of barium chloride is necessary only when free carbonic acid is titrated in the presence of alkali bicarbonates. Without it free alkali would then be formed: $NaHCO_3 + Ba(OH)_2 = BaCO_3 + H_2O + NaOH$.

† This method cannot be used when magnesium salts are present.

tion is colorless. From the amount of base used to absorb the carbon dioxide, the amount of the latter is calculated, 1 ml of N $Ba(OH)_2$ = 0.022 g CO_2 = 11.13 ml of CO_2 gas at 0° and 760 mm pressure.

Requirements. — 1. A calibrated bottle of 5-l capacity.

2. Standard solutions of barium hydroxide and hydrochloric acid. Prepare the acid so that 1 ml = 0.25 ml CO_2 at 0° C and 760 mm pressure; this is accomplished by diluting 224.7 ml of 0.1 N hydrochloric acid to 1 l. The barium hydroxide solution should be of about the same strength.

Procedure. — Place the dry bottle, with its capacity etched upon it, in the space from which the air is to be taken, and by means of a bellows, which is connected with a piece of rubber tubing reaching to the bottom of the bottle, change the air in the bottle by making about 100 strokes with the bellows. Stopper the bottle with a rubber cap, and note the temperature and barometer readings.

By means of a pipet, introduce 100 ml of barium hydroxide solution into the bottle, replace the rubber cap, and gently shake the solution back and forth in the flask for 15 minutes. Pour the turbid liquid into a dry flask, pipet out 25 ml, add phenolphthalein, and slowly run in hydrochloric acid with constant stirring until the solution is colorless. This requires n milliliters, so that for the 100 ml of base, $4 \times n$ milliliters would be necessary. Determine the strength of the barium hydroxide in terms of acid; 25 ml of barium hydroxide neutralize T milliliters of the standard hydrochloric acid, or 100 ml would neutralize $4 \times T$ milliliters of acid.

Calculation. — Assume the contents of the bottle to be V milliliters at $T°$ C and B millimeters pressure. By the introduction of 100 ml barium hydroxide solution the same volume of air was replaced, so that the amount of air taken for analysis amounts to $(V - 100)$ milliliters at $t°$ C and B millimeters. At 0° C and 760 mm pressure the volume is

$$V_0 = \frac{(V - 100)\,B \times 273}{760 \times (273 + t)}$$

100 ml of barium hydroxide solution require $4\ T$ milliliters HCl, while 100 ml of the alkali after treatment with V_0 milliliters of air require $4\ n$ milliliters of the acid and this corresponds to $4\,(T - n) \cdot 0.25 = (T - n)$ milliliters CO_2 at 0° C and 760 mm pressure.

The volume of CO_2 present in 1 l of air measured at standard conditions amounts to $1000 \cdot (T - n)$ milliliters of CO_2.

16. Persulfuric Acid

$$1000 \text{ ml of } 0.1\ N \text{ Potassium Hydroxide} = \frac{K_2S_2O_8}{20} = \frac{270.32}{20} = 13.52 \text{ g } K_2S_2O_8$$

If an aqueous solution of either potassium, sodium, or barium persulfate is boiled for some time, the salt is decomposed in accordance with the equation:

$$2\ K_2S_2O_8 + 2\ H_2O = 2\ K_2SO_4 + 2\ H_2SO_4 + O_2$$

into neutral sulfate and free sulfuric acid. The acid can be titrated with $0.1\ N$ potassium hydroxide solution.

Procedure. — Place about 0.25 g of the persulfate in an Erlenmeyer flask, dissolve in about 200 ml of water, and boil the solution for 20 minutes. Cool, add methyl orange, and titrate the solution with $0.1\ N$ potassium hydroxide. Or add an excess of the alkali and titrate with $0.1\ N$ acid.

The results correspond with those obtained by the ferrous sulfate method (cf. p. 572) provided the persulfate is not contaminated with potassium bisulfate.

Remark. — Ammonium persulfate cannot be analyzed by the above method because when a solution of this salt is boiled, two reactions take place. The principal reaction, to be sure, is

$$2\ (NH_4)_2S_2O_8 + 2\ H_2O = 2\ (NH_4)_2SO_4 + 2\ H_2SO_4 + O_2$$

but the oxygen is evolved to some extent in the form of ozone, which oxidizes a part of the nitrogen, so that besides sulfuric acid, the solution will contain more or less nitric acid:

$$8\ (NH_4)_2S_2O_8 + 6\ H_2O = 7\ (NH_4)_2SO_4 + 9\ H_2SO_4 + 2\ HNO_3$$

II. OXIDATION AND REDUCTION METHODS

Oxidation and reduction reactions are those in which the substance analyzed is either oxidized or reduced by means of the solution with which the titration is made. When hydrogen is oxidized by oxygen it is changed from the neutral condition to that of a positive valence (or polarity) of 1 and oxygen is reduced from the neutral condition to a negative valence (or polarity) of 2. In this, and all other cases, the equivalent weight of the element used in an oxidation-reduction reaction is the atomic weight divided by the change in polarity. When an atom in any complex molecule is subjected to a change in polarity (oxidized or reduced) the equivalent weight of the molecule is the gram-molecular weight divided by the *change in polarity* of the oxidized or reduced element. If more than 1 atom of the reactive element is present in the molecule, the molecular weight is divided by the total change in polarity, that is, by the change in polarity multiplied by the number of atoms undergoing such change (cf. p. 475).

COMMON OXIDIZING AGENTS

Reagent	Polarity Change	Gain in Electrons	Equivalent Weight
Cl_2	0 to −1	2 ϵ	$M/2$
Br_2	0 to −1	2 ϵ	$M/2$
I_2	0 to −1	2 ϵ	$M/2$
$K_2Cr_2O_7$	Cr^{VI} to Cr^{III}	6 ϵ	$M/6$
$KMnO_4$	Mn^{VII} to Mn^{++}	5 ϵ	$M/5$
$KMnO_4$	Mn^{VII} to Mn^{IV}	3 ϵ	$M/3$
$KBrO_3$	Br^{V} to Br^{-}	6 ϵ	$M/6$
KIO_3	I^{V} to I^{-}	6 ϵ	$M/6$
$KClO_3$	Cl^{V} to Cl^{-}	6 ϵ	$M/6$
Cu	Cu^{++} to Cu^{+}	1 ϵ	M
Na_2O_2	O_2^{--} to 2 O^{-2}	2 ϵ	$M/2$
concd. HNO_3	N^{V} to NO_2	1 ϵ	M
HNO_3	N^{V} to NO	3 ϵ	$M/3$
H_2O_2	O_2^{--} to 2 O^{-2}	2 ϵ	$M/2$

COMMON REDUCING AGENTS

Reagent	Polarity Change	Loss in Electrons	Equivalent Weight
$FeSO_4$ (or any ferrous salt)	Fe^{++} to Fe^{+++}	1 ϵ	M
$SnCl_2$	Sn^{II} to Sn^{IV}	2 ϵ	$M/2$
HI	I^{-} to I°	1 ϵ	M
Zn	Zn° to Zn^{++}	2 ϵ	$M/2$
H_2O_2	O_2^{--} to O_2°	2 ϵ	$M/2$
H_2S	S^{-2} to S°	2 ϵ	$M/2$
$C_2O_4^{--}$	$C_2O_4^{--}$ to 2 CO_2	2 ϵ	$M/2$
$S_2O_3^{--}$	$S_2O_3^{--}$ to $S_4O_6^{--}$	ϵ	M
$HAsO_3^{--}$	As^{III} to As^{V}	2 ϵ	$M/2$
SO_3^{--}	S^{IV} to S^{VI}	2 ϵ	$M/2$
As_2O_3	As^{III} to As^{V}	4 ϵ	$M/4$
$TiCl_3$	Ti^{III} to Ti^{IV}	1 ϵ	M
Fe	Fe° to Fe^{++}	2 ϵ	$M/2$
Fe dissolved in acid	Fe^{++} to Fe^{+++}	1 ϵ	M

Electrochemical Theory of Oxidation-Reduction

In considering the reactions of oxidation-reduction it is useful to prepare a table to show the relative strengths of the various oxidizing and reducing agents. Just as all acids and bases can be classified in a common table on the basis of the p_H values, so it is possible to prepare a single table which will show the tendency of each substance to undergo oxidation or reduction. Such a table can be called a *potential series.* It has been called a table of *oxidation potentials.* Just as we could use the concentration of OH^- as a basis of comparing dilute solutions of acids and bases instead of the concentration of H^+, because the product $[H^+] \times [OH^-]$ is equal to 10^{-14} in every solution at room temperature, so we can call the table one of *reduction potentials* since oxidation is just

the opposite to reduction and all we have to do is to change the sign. In some text-books, the same table is called one of *electrode potentials*. Whatever the table may be called, it is customary to place the strong reducing agents at the top of the table and end with the strong oxidizing agents. Thus, in considering the free elements with respect to their tendencies to undergo oxidation or reduction, we place the alkali metals at the top of the list and the non-metal oxygen followed by fluorine at the bottom.

It has already been pointed out that a substance is said to be oxidized or reduced when some atom it contains has undergone a change in polarity. Oxidation results when the polarity is increased, and reduction when the polarity is decreased. In terms of the electron theory, an increase in polarity means the loss of one or more electrons by an atom. Our definition of oxidation, therefore, has lost its original significance of necessarily having something to do with oxygen. The atom of oxygen is believed to consist of a nucleus around which eight electrons are circulating, probably in elliptical orbits. The path of the first two electrons, like that of the electrons around the helium nucleus, lies closer to the nucleus than that of the other six electrons, and we say that oxygen belongs in Family VI of the periodic table. When oxygen enters into combination with another element to form an oxide other than a peroxide, it accepts two electrons from the other element. Even if there is no ionization of the oxide molecule, it is reasonable to assume that the oxygen is negative with respect to the other element and that it has become negative by receiving electrons. Thus, in the water molecule, we are accustomed to think of the hydrogen as being positive to the oxygen although the electron of each hydrogen atom may be merely shared with the oxygen. Whenever, therefore, any atom gives up one or more of its electrons to some other atom, or even if it merely shares one or more of its electrons with some other atom, the atom to which the electron or electrons originally belonged is said to be oxidized and the element offered the electron is said to be reduced.

This electronic conception of oxidation and reduction makes it easy to see why an oxidation is always accompanied by a reduction. A transfer of electrons takes place whenever an electric current flows through an aqueous solution containing an electrolyte. At the anode, where electrons pass from the solution to the wire, some substance is oxidized. This oxidation may be the liberation of oxygen gas, the liberation of halogen gas, the dissolving of a metal electrode, the deposition of a higher oxide such as PbO_2 or MnO_2 upon the anode, or the oxidation of some substance present in the electrolyzed solution such as a ferrous salt. At the same time that an oxidation takes place at the anode, electrons

enter the solution at the cathode and a reduction takes place. This reduction may be the deposition of copper upon the cathode, the liberation of hydrogen gas, or the reduction of some substance in solution such as ferric salt, permanganate, or chromate. The only difference between oxidation and reduction that take place solely as a result of chemical reaction and oxidation and reduction during electrolysis is that they take place side by side in the chemical reaction whereas during electrolysis they may take place at some distance apart. Moreover, a chemical reaction of oxidation-reduction can be used as a source of an electric current.

If we place a piece of zinc in a solution of zinc sulfate and a piece of copper in a solution of copper sulfate and connect the two solutions by means of an inverted U-tube containing ammonium chloride solution, there will be no appreciable reaction until the copper and zinc are connected by a wire outside the solutions. Then a current will flow, electrons will pass from the wire to the solution and deposit copper, and electrons will leave the zinc and pass to the wire, forming zinc ions in the solution. The zinc, according to our definition, is oxidized and the copper is reduced; the two reactions take place simultaneously, and the effect is the same as if the piece of zinc were placed directly in the copper sulfate solution except that in that case we could not get any evidence of an electric current. So in precisely the same way we can produce an electric current by making use of the reaction between potassium dichromate and some substance that it oxidizes, such as hydrogen sulfide or ferrous chloride. To get the electric current in a wire, we must place the acid solution of dichromate in one vessel and the hydrogen sulfide or ferrous salt in another. We must provide some indifferent electrolyte between the two solutions, and place an insoluble electrode in each solution. Then, as soon as the electrodes are connected by a wire, a current will flow. The dichromate will be reduced in one vessel and the hydrogen sulfide or ferrous salt will be oxidized in the other, and the final effect will be exactly the same as if the dichromate solution were added directly to the solution of the ferrous salt.

The potential series of the elements, therefore, can be expanded to include almost every reaction of oxidation or reduction, although, to be sure, it is sometimes difficult to measure the electrode potentials and many of them are not known with any degree of exactness. The measurement of the potentials is usually accomplished by measuring the potential difference between two electrodes choosing as one electrode a standard half-cell of definitely known potential.

These potentials enable one to predict whether a given oxidation is likely to take place to completion so that it can be used in quantitative

analysis. They do not tell, however, whether the speed of the reaction is sufficiently high to make the process satisfactory. Thus permanganate should be able to oxidize the reduced forms of substances listed about 0.15 volt higher in the table, but often the reaction takes place too slowly, as in the reaction with oxalic acid at room temperature. The presence of a catalyst is often needed.

The mass-action law applies to every oxidation-reduction reaction, and it is important that the beginner should understand such application. The potential of a metal against a solution of its ions is governed by the mathematical expression

$$E_{18} = E_0 - \frac{0.058}{n} \log c$$

when E_{18} is the observed electrode potential at 18°, E_0 is the potential given in the table (corresponding to the potential of the metal in a molal solution of its ions), n is the change in polarity, and c is the concentration of the ions expressed in moles per liter. The value 0.058 is a constant which varies with the absolute temperature; at 25° it is 0.059. The equation shows that the observed potential goes upward by 0.058 volt for a change of valence of one, or 0.029 volt for a valence change of two, when the concentration of the ions in the solution is 0.1 molal instead of molal. This means that the metal is easier to oxidize when the solution does not contain many of its ions and harder to deposit by electrolysis.

The student may notice that the above equation is often written with a positive sign on the right-hand side. This is because physicists and many chemists are accustomed to call the potentials negative at the top of the table and positive at the bottom with hydrogen at 0.00. It is purely arbitrary whether a given potential is called positive or negative with respect to hydrogen, and depends entirely on the definition of what is meant by positive. The chemist usually thinks of the elements at the top of the column as positive elements, but in making up an electrolytic cell, the positive to negative direction of the current in the wire is always from the lower to the higher member of the series. Thus in the Daniell cell, the physicist considers the zinc immersed in zinc sulfate solution as the negative element and the copper immersed in copper sulfate solution as the positive element. Zinc is positive to copper in the solution, and copper is positive to zinc in the wire. In this book, therefore, the potentials given are reduction potentials, and if the sign before each value is changed the table becomes one of oxidation potentials. In the latter case the above equation becomes

$$E_{18} = E_0 + \frac{0.058}{n} \log c \quad \text{or} \quad E_{18} = E_0$$

The following table gives the reduction potentials of some of the common substances which easily undergo oxidation or reduction. Some of the potentials are not known exactly, but the relative position in the

NORMAL REDUCTION POTENTIALS

Oxidized Form	Reduced Form	Change in Polarity	Electrode Reaction	Normal Potential or E_0 in Volts
K^+	K	1	$K^+ + e \rightleftarrows K$	2.92
Ca^{++}	Ca	2	$Ca^{++} + 2e \rightleftarrows Ca$	2.9
Mg^{++}	Mg	2	$Mg^{++} + 2e \rightleftarrows Mg$	2.40
Zn^{++}	Zn	2	$Zn^{++} + 2e \rightleftarrows Zn$	0.76
Fe^{++}	Fe	2	$Fe^{++} + 2e \rightleftarrows Fe$	0.43
H^+	$\frac{1}{2} H_2$	1	$H^+ + e \rightleftarrows \frac{1}{2} H_2$	0.00
SO_4^{--}	S^{--}	8	$SO_4^{--} + 8H^+ + 6e \rightleftarrows S + 4H_2O$	?
Ti^{++++}	Ti^{+++}	1	$Ti^{++++} + e \rightleftarrows Ti^{+++}$	−0.04
S°	S^{--}	2	$S^\circ + 2e \leftarrow S^{--}$	−0.09?
SO_4^{--}	SO_3^{--}	2	$SO_4^{--} + 2e \rightleftarrows SO_3^{--}$	?
$\frac{1}{2} S_4O_6^{--}$	$S_2O_3^{--}$	1	$\frac{1}{2} S_4O_6^{--} + e \rightleftarrows S_2O_3^{--}$	−0.13
Sn^{++++}	Sn^{++}	2	$Sn^{++++} + 2e \rightleftarrows Sn^{++}$	−0.14
Cu^{++}	Cu	2	$Cu^{++} + 2e \rightleftarrows Cu$	−0.34
UO_2^{++}	U^{++++}	2	$UO_2^{++} + 4H^+ + 2e \rightleftarrows U^{++++} + 2H_2O$	−0.36
Cu^{++}	Cu^+	1	$Cu^{++} + 2Cl^- + e \rightleftarrows CuCl_2^-$	−0.46
$Fe(CN)_6^{---}$	$Fe(CN)_6^{----}$	1	$Fe(CN)_6^{---} + e \rightleftarrows Fe(CN)_6^{----}$	−0.49
CO_2	$C_2O_4^{--}$	2	$2CO_2 + 2e \leftarrow C_2O_4^{--}$	?
$\frac{1}{2} I_2$	I^-	1	$\frac{1}{2} I_2 + e \rightleftarrows I^-$	−0.54
H_3SbO_4	H_3SbO_3	2	$\left\{\begin{array}{l} H_3SbO_4 + 5H^+ + 2e \rightarrow Sb^{+++} + 4H_2O \\ H_3SbO_4 + H_2O + 2e \leftarrow H_3SbO_3 + 2OH \end{array}\right.$	?
H_3AsO_4	H_3AsO_3	2	$H_3AsO_4 + 2H^+ + 2e \rightleftarrows H_3AsO_3 + H_2O$	−0.57
HNO_2	NO	1	$NO_2^- + 2H^+ + e \rightleftarrows NO + H_2O$	−0.7?
Fe^{+++}	Fe^{++}	1	$Fe^{+++} + e \rightleftarrows Fe^{++}$	−0.75
HVO_3	VO^{++}	1	$VO_3^- + 4H^+ + e \rightleftarrows VO^{++} + 2H_2O$	−0.92
Dil. HNO_3	HNO_2	2	$NO_3^- + 2H^+ + 2e \rightleftarrows NO_2^- + H_2O$	−0.9
Conc. HNO_3	NO_2	1	$NO_3^- + 2H^+ + e \rightleftarrows NO_2 + H_2O$	?
IO_3^-	I^-	6	$IO_3^- + 6H^+ + 6e \rightleftarrows I^- + 3H_2O$	−1.02?
$\frac{1}{2} Br_2$	Br	1	$\frac{1}{2} Br_2 + e \rightleftarrows Br^-$	−1.07
O_2	H_2O_2	2	$O_2 + 2H^+ + 2e \rightleftarrows H_2O_2$	−1.08
$Cr_2O_7^{--}$	$2Cr^{+++}$	6	$Cr_2O_7^{--} + 14H^+ + 6e \rightleftarrows 2Cr^{+++} + 7H_2O$	−1.3
MnO_2	Mn^{++}	2	$MnO_2 + 4H^+ + 2e \rightleftarrows Mn^{++} + 2H_2O$	−1.33
$\frac{1}{2} Cl_2$	Cl^-	1	$\frac{1}{2} Cl_2 + e \rightleftarrows Cl^-$	−1.36
Ce^{++++}	Ce^{+++}	1	$Ce^{++++} + e \rightleftarrows Ce^{+++}$	−1.45
BrO_3^-	Br^-	6	$BrO_3^- + 6H^+ + 6e \rightleftarrows Br^- + 3H_2O$	−1.48
MnO_4^-	Mn^{++}	5	$MnO_4^- + 8H^+ + 5e \rightleftarrows Mn^{++} + 4H_2O$	−1.52
MnO_4^-	MnO_2	3	$MnO_4^- + 4H^+ + 3e \rightleftarrows MnO_2 + 2H_2O$	−1.58
$S_2O_8^{--}$	$2SO_4^{--}$	2	$S_2O_8^{--} + 2e \rightleftarrows 2SO_4$	?
H_2O_2	H_2O	2	$H_2O_2 + 2H^+ + 2e \rightleftarrows 2H_2O$	−1.9
$NaBiO_3$	Bi^{+++}	2	$NaBiO_3 + 6H^+ + 2e \rightarrow Na^+ + Bi^{+++} + 3H_2O$	?
$\frac{1}{2} F_2$	F^-	1	$\frac{1}{2} F_2 + e \rightleftarrows F^-$	−2.8

table is approximately that given. The values of E_0 are for the case when the concentrations of both the oxidized and reduced forms are equal to 1 molal. If the hydrogen ion enters into the reaction, the values correspond to the presence of sufficient hydrogen ions to make the solution molal. The concentration of water is assumed to be constant and not changed appreciably by the progress of the reaction. The letter e in the equilibrium expressions represents a "gram-electron" or electricity corresponding to 1 faraday = 96,500 coulombs or 26.82 ampere-hours.

The electrode reaction for a simple case of oxidation-reduction in which no other substance participates can be written

$$Ox + n\,e \rightleftarrows Red$$

when Ox represents the oxidized form, Red, the reduced form, n the change in polarity, and e the electron (faraday in case of the gram-atom). The equilibrium between a metal and its ions is a special case in which the metal represents the reduced form, and since the metal as such is insoluble in water, its concentration does not enter into consideration. The equilibrium is the same whether we take a wire or a thick rod of the metal. If, however, the substance exists to an appreciable extent dissolved in the solution, the concentration of both Ox and Red has an effect upon the final state of equilibrium. Expressing these concentrations in moles per liter as $[Ox]$ and $[Red]$, the expression for the normal potential becomes

$$E_{18} = E_0 - \frac{0.058}{n} \log \frac{[Ox]}{[Red]}$$

The value E_0 is that given in the table where it is assumed that each concentration is that of a molal solution. Then since $[Ox] = [Red]$ and the log of $1 = 0$, the second term disappears and $E_{18} = E_0$.

If hydrogen or hydroxyl ions take part in the reaction they also influence the final state of equilibrium. Thus, in the reaction $H_3AsO_4 + 2\,H^+ + 2\,e \rightleftarrows H_3AsO_3 + H_2O$, the potential is determined by the equation:

$$E_{18} = E_0 - \frac{0.058}{2} \log \frac{[H_3AsO_4]\,[H^+]^2}{[H_3AsO_3]}$$

and in the reaction $MnO_4^- + 8\,H^+ + 5\,e \rightleftarrows Mn^{++} + 4\,H_2O$ the potential is determined by the equation

$$E_{18} = E_0 - \frac{0.058}{5} \log \frac{[MnO_4^-]\,[H^+]^8}{[Mn^{++}]}$$

In these last two cases it is not necessary to take the H_2O into consideration because when the reaction takes place in a dilute solution the concentration of the water does not change appreciably as a result of the progress of the oxidation and reduction. The concentration of the hydrogen ions determines the final state of equilibrium to a marked degree in the above reactions. Thus, in a strongly acid solution, arsenic acid can be reduced quantitatively to arsenious acid by means of potassium iodide, but in a slightly alkaline solution, arsenite can be oxidized completely to arsenate by iodine. The above arsenate-arsenite equation can be written

$$\cdot \frac{0.058}{2} \log \frac{[H_3AsO_4]}{[H_3AsO_3]} \quad \cdot \frac{0.058}{2} \log [H]^2$$

and in this form can be used to calculate the effect of changes in hydrogen-ion concentration or to calculate the effect of changes in the $[H_3AsO_4]$ to $[H_3AsO_3]$ ratio at a definite concentration of hydrogen ions.

With permanganate, the reduction products are different at different concentrations of hydrogen ions. Thus in acid solutions, Mn^{++} is the usual product; in neutral or slightly alkaline solutions MnO_2 is usually formed; and in strongly alkaline solutions green MnO_4^{--} is sometimes obtained.

OXIDATION METHODS

A. Potassium Permanganate Methods

Manganese, from the standpoint of oxidation-reduction reactions, is an interesting element. The potentials relating to the various valence states are given in the following table:

	Reaction	Volts
(*a*)	$\mathbf{Mn} = Mn^{++} + 2\,\epsilon$	+1.1
(*b*)	$MnO_4^{--} = MnO_4^{-} + \epsilon$	−0.66
(*c*)	$\mathbf{MnO_2} + 4\,OH^{-} = MnO_4^{-} + 2\,H_2O + 3\,\epsilon$	−0.69
(*d*)	$\mathbf{MnO_2} + 4\,OH^{-} = MnO_4^{--} + 2\,H_2O + 2\,\epsilon$	−0.71
(*e*)	$Mn^{+++} + 2\,H_2O = \mathbf{MnO_2} + 4\,H^{+} + \epsilon$	−1.2
(*f*)	$Mn^{++} + 2\,H_2O = \mathbf{MnO_2} + 4\,H^{+} + 2\,\epsilon$	−1.33
(*g*)	$Mn^{++} = Mn^{+++} + \epsilon$	−1.5
(*h*)	$Mn^{++} + 4\,H_2O = \quad + 8\,H^{+} + 5\,\epsilon$	−1.52
(*i*)	$\mathbf{MnO_2} + 2\,H_2O = MnO_4^{-} + 4\,H^{+} + 3\,\epsilon$	−1.63

In the table, the Greek letter ϵ signifies the electron, or the transfer of one faraday (96,500 coulombs) if the gram-atom or gram-molecule is understood. Black-faced type signifies that the substance as such is insoluble.

The formation of a manganous salt from metallic manganese is indicated by equation (*a*). The normal potential of 1.1 volts indicates that the metal is oxidized a little more easily than zinc and somewhat less readily than aluminum (which is unprotected by an oxide film). Dilute acids, therefore, dissolve the metal with

evolution of hydrogen and formation of bivalent manganous salt. Nitric acid, aqua regia, or halogens in the presence of a strong acid are incapable of oxidizing the manganous salt. The bivalent manganous salts, although slightly colored in the form of hydrated crystals, yield colorless solutions.

Salts of trivalent manganese, called manganic salts, are known but they are not very stable. Equation (*e*) shows that it is possible under some conditions to form a manganic salt from manganese dioxide and leads one to expect that it ought to be possible to oxidize a manganic salt to manganese dioxide in the presence of alkali hydroxide or the salt of a weak acid, because, since hydrogen ions are liberated when manganic salt is oxidized, the reaction should take place more readily if the hydrogen ions are removed as fast as they are formed. The potential of reaction (*g*) in the table indicates that manganic salts are easily reduced to manganous salts in the presence of acid.

Some salts of quadrivalent manganese are known. Thus, cold concentrated hydrochloric acid will slowly dissolve manganese dioxide, forming manganese tetrachloride. Complex salts, such as K_2MnF_6 and K_2MnCl_6, have been prepared. These salts, however, are not stable and are of little interest to the analytical chemist. The dioxide, MnO_2, occurs in nature as the mineral pyrolusite which is the most important source of all manganese compounds and can be regarded as the anhydride of manganous acid, H_2MnO_3, which is known to have salts called manganites. The potential of reaction (*c*) in the above table indicates that it ought to be possible to form MnO_4^- from MnO_2, and conversely that MnO_2 can be expected to be formed as a reduction product when permanganate acts as an oxidizer. Potassium permanganate is much used for the oxidation of many organic compounds in neutral or alkaline solutions, and MnO_2 is the reduction product that is usually formed. The potential of reaction (*d*) shows that MnO_2 in alkaline solution should be convertible into a manganate, such as Na_2MnO_4. All manganese oxides, on being fused with caustic alkali or alkali carbonate in the air or in the presence of some oxidizing agent such as potassium nitrate, are converted into green alkali manganate, and this reaction has frequently been used as a sensitive test for manganese. Usually the precipitate of manganous hydroxide produced by adding sodium hydroxide to the solution of a manganous salt is fused with sodium carbonate on platinum, and if the melt assumes a green color, the presence of manganese is indicated. The potential of reaction (*f*) shows that manganese dioxide is a good oxidizing agent, and this corresponds to the fact that we can dissolve it by treating with acid and any good reducing agent, such as a ferrous salt, an oxalate, a sulfite, or hydrogen peroxide. With hot concentrated hydrochloric acid, chlorine is formed.

$$\mathbf{MnO_2} + 2\,Fe^{++} + 4\,H^+ = Mn^{++} + 2\,Fe^{+++} + 2\,H_2O$$
$$\mathbf{MnO_2} + C_2O_4^{--} + 4\,H^+ = Mn^{++} + 2\,CO_2 + 2\,H_2O$$
$$\mathbf{MnO_2} + H_2O_2 + 2\,H^+ = Mn^{++} + O_2 + 2\,H_2O$$
$$\mathbf{MnO_2} + 2\,HCl = MnCl_2 + Cl_2$$

Aside from its characteristic color and use as a qualitative test, the green manganate anion MnO_4^{--} is of little interest to the analytical chemist. Equations (*h*) and (*i*), however, show that the reduction potential of the manganate anion is close to that of the permanganate anion. Sometimes, in the analysis of duplicate samples, the chemist finds after an oxidation treatment that one sample is green, showing the presence of manganate, and the other is purple owing to the formation of permanganate.

Permanganate ions, MnO_4^-, have such a strong color that a single drop of a tenth-normal permanganate solution will impart a perceptible color to 500 ml of

another solution. Permanganate, therefore, is its own indicator. In most oxidations with permanganate that take place in acid solutions, the permanganate anion is reduced to colorless manganous cations and the reduction potential of the permanganate under those conditions is shown by equation (*h*) in the table on p. 543. In a nearly neutral solution, however, permanganate is capable of oxidizing manganous ions to the quadrivalent state, to which it is itself reduced. This is the so-called *Volhard* titration.

$$3\ Mn^{++} + 2\ MnO_4^- + 2\ H_2O = 5\ \mathbf{MnO_2} + 4\ H^+$$

The potential values given on p. 543 should not be regarded as absolutely accurate. The measurement of some of these potentials is difficult, and sometimes it is hard to prevent some side reaction from taking place. The work performed in any chemical reaction of oxidation-reduction can be measured in joules or watt-seconds, that is, by multiplying the quantity of electricity involved by the voltage shown. If manganese from any valence is converted into manganese at some other valence, the work performed is theoretically the same whether the oxidation takes place all at once or in several stages. This enables one to compute some of the potential values in the table on p. 543 from other values that are given. In making such computations, the signs before the voltages in the table merely indicate which direction the current is moving; it is purely arbitrary whether the signs are made positive or negative, and physicists in general use the opposite signs to those given in the table because they are thinking of the direction of the current in the wire whereas the chemist is thinking of the direction of the current in the solution, as has already been pointed out. To show how computations can be made, the following illustration will serve:

Reaction (*f*) on p. 543 represents the oxidation of bivalent manganese to the quadrivalent state. Reaction (*i*) covers the oxidation of quadrivalent manganese to the septavalent state, and reaction (*h*) the oxidation of bivalent manganese directly to the septavalent state. In other words, reaction (*h*) represents the sum of reactions (*f*) and (*i*), and the work done is theoretically the same whether the reaction takes place in the two stages or all at once.

Energy is composed of two factors, an intensity factor and a capacity factor. The work done is measured by the product of these two factors. Thus, in measuring the work done in compressing a gas, we must take into consideration the change in volume (capacity factor) and the pressure (intensity factor), and the work done is measured by multiplying the pressure by the volume. In electrical units, the work done is measured by multiplying the amount of electricity moving (expressed in coulombs, ampere-seconds, or ampere-hours, etc.) and the potential difference (expressed in volts). In all the reactions given in the table on p. 543, therefore, the work done or, as it is sometimes expressed, the change in the *free energy*, is proportional to the number of electrons liberated multiplied by the voltage shown. Thus in equation (*a*) the work done is proportional to the product 2×1.1. In the oxidation of a gram-atom of manganese from the metallic to the manganous state, two faradays of electricity ($2 \times 96{,}500$ coulombs or ampere-seconds or 2×26.82 ampere-hours) are involved, and the potential drop is 1.1 volt.

Then, with respect to equations (*f*), (*i*), and (*h*) in the table on p. 543, if we call the respective voltages v_1, v_2, and v_3, we have

$$2\ v_1 + 3\ v_2 = 5\ v_3$$

and if two of these values are known, the third can be computed. In such computations, it should be borne in mind that none of the values given in the table is to be

regarded as absolutely correct. Whatever errors there may be in the values given for v_1, v_2, and v_3 are multiplied by 2, 3, and 5, respectively, so that the result of the calculation may differ a little from the value given. Thus

$$2 \times -1.33 + 3 \times -1.63 = -7.55$$

but 5 times the value given for v_3 in the table is $5 \times -1.52 = 7.60$, and this is as near as such computations can be expected to check. In this particular case, it is well to note that reaction (*h*) is the sum of reactions (*f*) and (*i*) and not the sum of reactions (*c*) and (*f*). Reaction (*c*) is very similar to reaction (*i*) but refers to a solution which is normal in OH^- whereas the latter refers to one which is normal in H^+.

When potassium permanganate acts as an oxidizing agent in distinctly acid solution, the manganese is reduced from a positive valence of 7 to a positive valence of 2 — the manganese atom accepts 5 electrons from the substance oxidized:

$$MnO_4^- + 8\ H^+ + 5\ \epsilon = Mn^{++} + 4\ H_2O$$

The equivalent weight of potassium permanganate, or the quantity required to make 1 l of normal solution, is, therefore, one-fifth of the molecular weight. In many reactions which take place in neutral or alkaline solutions, a precipitate of manganese dioxide is formed corresponding to a reduction to the quadrivalent state, but since a solution of potassium permanganate is usually standardized in acid solution with complete reduction of the manganese to the bivalent state, it is customary to express the normality of permanganate on this basis.

The following equations represent the action of permanganate on some of the common substances which are oxidized quantitatively by it:

$$MnO_4^- + 5\ Fe^{++} + 8\ H^+ = Mn^{++} + 5\ Fe^{+++} + 4\ H_2O$$
$$2\ MnO_4^- + 5\ C_2O_4^{--} + 16\ H^+ \rightarrow 2\ Mn^{++} + 10\ CO_2 + 8\ H_2O$$
$$2\ MnO_4^- + 5\ Sn^{++} + 16\ H^+ \rightarrow 2\ Mn^{++} + 5\ Sn^{++++} + 8\ H_2O$$
$$2\ MnO_4^- + 10\ I^- + 16\ H^+ \rightarrow 2\ Mn^{++} + 5\ I_2 + 8\ H_2O$$
$$2\ MnO_4^- + 3\ Mn^{++} + 2\ H_2O \rightarrow 5\ MnO_2 + 4\ H^+$$
$$2\ MnO_4^- + 5\ H_2O_2 + 6\ H^+ \rightarrow 2\ Mn^{++} + 8\ H_2O + 5\ O_2 \uparrow$$

When potassium permanganate acts as an oxidizing agent in distinctly acid solution, the manganese is reduced from a valence of +7 to +2, corresponding to a loss of 5 charges in polarity. A normal solution of permanganate, therefore, contains $\frac{1}{5}$ mole of $KMnO_4$ = 31.61 g.

For most oxidation analyses 0.1 *N* and rarely 0.5 *N* solutions are used.

The Preparation of 0.1 *N* Potassium Permanganate Solution

was described on p. 101.

Standardization of Permanganate Solution

1. *Against Sodium Oxalate* (Sörensen)*

1000 ml of 0.1 *N* permanganate solution = 6.700 g $Na_2C_2O_4$

Sodium oxalate suitable for standardizing solutions can be obtained from the Bureau of Standards at Washington, D. C. This is the most

* *Z. anal. Chem.*, **42**, 352, 512 (1903); **45**, 272 (1906).

reliable standard of all those that have been proposed. Dry the sample for an hour at 130°. For the standardization McBride recommends* the following procedure.

In a 400-ml beaker, dissolve 0.25–0.3 g of sodium oxalate in 200–250 ml of hot water (80–90°) and add 10 ml of 18 N sulfuric acid. Titrate at once with 0.1 N $KMnO_4$ solution, *stirring the liquid vigorously and continuously.* The permanganate must not be added more rapidly than 10–15 ml per minute, and the last 0.5–1 ml must be added dropwise with particular care to allow each drop to be fully decolorized before the next is introduced. The excess of permanganate used to cause an end-point color should be estimated by matching the color in another beaker containing the same bulk of acid and hot water. The temperature of the solution should not be below 60° by the time the end point is reached; more rapid cooling may be prevented by allowing the beaker to stand on a small asbestos-covered hot plate during the titration. The use of a small thermometer as stirring-rod is most convenient in these titrations, as the variation of temperature is then easily observed.

Two positive charges are required to oxidize the $C_2O_4^{=}$ ion to CO_2 gas.

$$C_2O_4^{=} - 2\,\epsilon = 2\,CO_2$$

It is evident, therefore, that the equivalent weight of the oxalate anion acid is $\frac{1}{2}$ mole.

2. *Against Oxalic Acid*

Owing to its water of crystallization, oxalic acid, $H_2C_2O_4{\cdot}2H_2O$ is not as reliable a standard as the sodium salt. Its equivalent weight is $\frac{1}{2}$ mole = 63.03, the same as when it acts as an acid.

It is sometimes desirable to check up the oxidimetric and alkalimetric standards; and oxalic acid, potassium binoxalate, and potassium tetroxalate either as dry salt or in solution can serve for this purpose. The method of titrating is the same as in 1. The equivalent weights of these three substances are quite similar as reducing agents but very different as acids. Thus in a liter of aqueous solution the tabulated relationships hold.

Weight per liter	Normality as Acid	Normality as Reducer
0.5 mole = 63.03 g $H_2C_2O_4{\cdot}2H_2O$	1 N	1 N
0.5 mole = 64.06 g KHC_2O_4	0.5 N	1 N
0.25 mole = 63.54 g $KHC_2O_4{\cdot}H_2C_2O_4{\cdot}2H_2O$	0.75 N	1 N

* *J. Am. Chem. Soc.*, **34**, 393 (1912).

3. *Against Metallic Iron*

It was formerly the general practice to standardize against iron wire, particularly when the standard solution ... used for the titration of iron ores. The practice is not to be mended because of the readiness with which the material rusts because a low carbon content influences the results, not always in the same way. If, however, a solution of permanganate is standardized against sodium oxalate and also against iron wire, then the *apparent* iron value of the wire is known and it can be used as a standard. The method is as follows.

Weigh out 0.2 g of the wire into a 200–250-ml flask as shown in Fig. 111. Displace the air by introducing a stream of carbon dioxide, which has passed through a bottle containing water and another containing copper sulfate solution (to remove H_2S). Dissolve the wire in 55 ml of $3.6N$ sulfuric acid. During the dissolving of the wire, support the

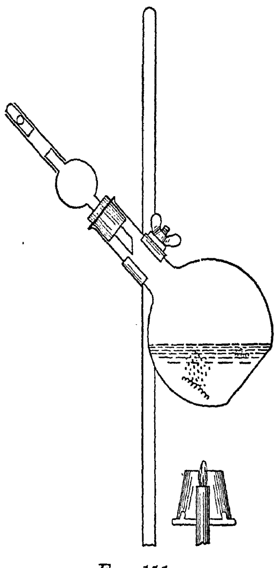

FIG 111.

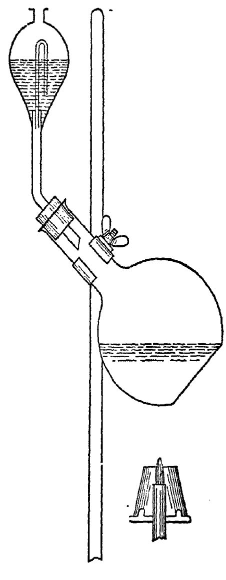

FIG. 112.

flask as shown in the drawing, and with the gas-exit tube closed with a rubber stopper which is connected with a Bunsen valve.* Heat the

* A Bunsen ...

contents of the flask by means of a low flame until the wire has all dissolved, then boil the solution gently for a short time. Allow to cool, remove the stopper, and titrate with permanganate.

Instead of using a Bunsen valve, the Contat-Göckel valve may be used as shown in Fig. 112. The funnel contains a cold, saturated solution of sodium bicarbonate, through which the hydrogen from the flask passes. When the flame is removed sodium bicarbonate solution is drawn into the flask, and this causes the evolution of carbon dioxide, which prevents the entrance of more of the solution.

4. *Against Sodium Thiosulfate*

See Iodometry.

5. *Against Hydrogen Peroxide*

See Gas Analysis.

6. *Against Ferrous Ammonium Sulfate*

$$(NH_4)_2SO_4 \cdot FeSO_4 \cdot 6H_2O$$

Mohr proposed the use of this salt as a standard and it can be purchased in a high state of purity. The equivalent weight is 392.14 or nearly 6 times as large as that of sodium oxalate. This makes it easier to weigh out a sample accurately to 4 significant figures. The substance is not as reliable a standard because of the danger of losing water of crystallization and of oxidizing. Thus a sample weighed out and allowed to stand in a moist beaker for some time is likely to undergo partial oxidation. The best way to determine whether a sample is suitable is to check up the standardization values obtained with this substance and with sodium oxalate. The gravimetric determination of the iron content is likely to lead to error; usually the values for iron are found a little too high and this gives low results in the standardization.

Procedure. — For the standardization of 0.1 N permanganate, weigh out samples of about 1.5 g to 4 significant figures. Add 10 ml of 18 N sulfuric acid, dilute to 100 ml, and at once titrate.

Permanence of Potassium Permanganate Solutions

A *pure* permanganate solution will keep indefinitely, provided it is kept free from dust and reducing vapors.* For very accurate work,

which is sealed at one end, and has a hole on one side. This tube serves to prevent the collapse of the rubber tubing at the place where the slit is formed.

* In June, 1899, 1 ml of a $KMnO_4$ solution = 0.005485 g Fe; in March, 1900, 1 ml of the $KMnO_4$ solution = 0.005476 g Fe. See also Morse, Hopkins, and Walker, *Am. Chem. J.*, **18**, 401.

however, it is advisable to standardize the solution frequently. The addition of 10 g caustic potash per liter increases the stability of the solution.

USES OF PERMANGANATE SOLUTION

1. Determination of Iron

(a) Method of Margueritte (1846)

$$1 \text{ ml of } 0.1\,N\ KMnO_4 \text{ corresponds to } \begin{cases} 0.005584 \text{ g Fe} \\ 0.007184 \text{ g FeO} \\ 0.007984 \text{ g } Fe_2O_3 \end{cases}$$

In this determination the iron is oxidized from the ferrous to the ferric condition:

$$2\,KMnO_4+10\,FeSO_4+8\,H_2SO_4=K_2SO_4+2\,MnSO_4+5\,Fe_2(SO_4)_3+8\,H_2O$$

To each 100 ml of the ferrous salt solution add 5 ml of sulfuric acid, and at a volume of about 400 ml titrate in the cold by adding potassium permanganate from a buret with glass stopcock until a permanent pink color is obtained.

This determination affords very accurate results and is unquestionably one of the best methods for determining iron.

TITRATION OF FERROUS SALTS IN HYDROCHLORIC ACID SOLUTION

The titration of iron in hydrochloric acid solution gives high results unless particular precautions are taken. If dilute permanganate solution is allowed to run into a cold dilute solution of ferrous chloride containing hydrochloric acid, the permanganate is decolorized and the iron is oxidized, but there is noticeable evolution of chlorine.* More permanganate is used than is necessary to oxidize the ferrous salt to the ferric condition.

If, however, permanganate is run into cold, dilute hydrochloric acid, in the absence of ferrous salt, there is no evolution of chlorine. Furthermore, the presence of a ferric salt does not cause evolution of chlorine. The chlorine, therefore, is not a result of the direct action of the permanganate upon the hydrochloric acid, but is probably due to the oxidation of the ferrous ion to an unstable state of oxidation corresponding to a perchloride, a peroxide, ferric acid, or perferric acid.

When permanganate is run into a dilute hydrochloric acid solution containing ferrous chloride and considerable manganous salt, the fer-

* Löwenthal and Lenssen, *Z. anal. Chem.*, **1863**, 329.

rous iron is oxidized quantitatively to ferric iron and there is *no evolution of chlorine.* This was shown by Kessler* in 1863 and by Zimmermann† in 1881. It has since been confirmed by many other chemists.‡

This can be explained as follows: Permanganate ions react with manganous ions to form, as Volhard§ proved, quadrivalent manganese. In this state of oxidation, manganese is unstable in acid solution, but it is reduced more readily by ferrous ions than by chloride ions.

Zimmermann|| suspected, and Manchot's¶ experiments confirm this view, that iron like manganese has a tendency to form unstable compounds as primary oxidation products. If such a compound is formed in the presence of manganous ions, the iron will give up its excess charge to manganous rather than to chloride ions, provided sufficient manganous ions are present.

According to Manchot there is a tendency in all oxidations to form an unstable compound as the primary oxidation product. When hydrogen burns in air, a little hydrogen peroxide is formed; when sodium burns, sodium peroxide results. In most cases, these primary products are unstable and cannot be isolated because of the readiness with which they are reduced to a more stable condition. When an *acceptor*** is present it will take up the excess charge which is lost when the primary product is reduced; in aqueous solutions in the absence of any other acceptor, free oxygen is evolved.

According to the method of oxidation, iron tends to form different primary states of oxidation. In the direct oxidation of iron by oxygen, the primary oxide appears to be FeO_2; in the oxidation by means of permanganate, chromic acid, or hydrogen peroxide, the primary oxidation product appears to contain iron with a valence of 5, whereas iron with a valence of 6 is probably formed if hypochlorous acid is the oxidizer.

Potassium permanganate according to Manchot first causes the formation of quinquevalent iron. If sufficient manganese ions are present, these play the part of acceptor, but otherwise, in hydrochloric acid solution, some chlorine is formed:

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* *Pogg, Ann.*, **118**, 779, and **119**, 225.

† *Ber.*, **14**, 779, and *Ann. Chem. Pharm.*, **213**, 302.

‡ For example, J. A. Friend, *J. Chem. Soc.*, **95**, 1228 (1909). C. C. Jones and J. H. Jeffery, *The Analyst*, **34**, 306 (1909).

§ *Ann. Chem. Pharm.*, **198**, 337.

|| *Ber.*, **11**, 779, and *Ann. Chem. Pharm.*, **213**, 302.

¶ *Ann. Chem. Pharm.*, **325**, 105 (1902).

** An *acceptor* is a substance which is not oxidized by oxygen alone, but can be oxidized by the aid of some other substance present called an *auto-oxidator*. A substance which tends to be peroxidized may play the part of an acceptor. Cf. Engler, *Ber.*, **33**, 1097 (1900).

$$3\,MnO_4^- + 5\,Fe^{++} + 24\,H^+ \rightarrow 3\,Mn^{++} + 5\,Fe^{\overset{+++}{++}} + 12\,H_2O$$

$$Fe^{\overset{+++}{++}} + Mn^{++} \rightarrow Mn^{\overset{++}{++}} + Fe^{+++}$$

$$Mn^{\overset{++}{++}} + 2\,Fe^{++} \rightarrow Mn^{++} + 2\,Fe^{+++}$$

$$Fe^{\overset{+++}{++}} + 2\,Cl^- \rightarrow Cl_2 + Fe^{+++}$$

The action of the manganous sulfate is partly to regulate the reaction between ferrous and permanganate ions, for, according to Volhard, the manganous ions tend to react with permanganate, thus slowing down the reaction between permanganate and ferrous ions. The quadrivalent manganese formed by the action of permanganate on manganous ions, at once reacts with ferrous ions; the manganous ions also act as acceptor toward any iron oxidized above the trivalent state. In both cases it is essential that manganese peroxide does not react with hydrochloric acid very rapidly, and it is necessary, too, that the amount of manganous salt shall greatly exceed the amount of iron present.

Although it is possible, then, to titrate iron in hydrochloric acid solutions in the presence of manganous sulfate, the method possesses the disadvantage that the end point cannot be seen so distinctly as when no chloride is present, since ferric chloride forms a much more yellow solution than does ferric sulfate. This difficulty can be overcome by the addition of phosphoric acid, as suggested by C. Reinhardt.*

(*b*) Method of Zimmermann-Reinhardt

Add 20–25 ml of manganese sulfate solution (prepared as described below) to a solution of ferrous chloride containing about 15 ml of 6 *N* hydrochloric acid, dilute to 300 ml, and titrate the cold solution with potassium permanganate added so slowly that the drops can be counted.

Take care toward the last not to add a drop of permanganate until the color of the preceding one has disappeared.

Prepare the manganous sulfate solution as follows: Dissolve 67 g of crystallized manganous sulfate ($MnSO_4 \cdot 4H_2O$) in 500–600 ml of water, add 138 ml of phosphoric acid (*d.* 1.7) and 130 ml of concentrated sulfuric acid; dilute the mixture to 1 l.

If the iron is present as ferric salt, it must be reduced completely to the ferrous condition before it can be titrated with potassium permanganate.

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* *Stahl und Eisen*, **1884**, 709, and *Chem. Ztg.*, **13**, 323.

REDUCTION OF FERRIC SALTS TO FERROUS SALTS

The reduction of ferric to ferrous salts can be accomplished in a number of different ways.

1. *By Hydrogen Sulfide*

Saturate the solution with hydrogen sulfide and boil off the excess while introducing CO_2 into the solution which is contained in a flask.

2. *By Sulfur Dioxide*

Nearly neutralize the solution containing the ferric salt with sodium carbonate,* add an excess of sulfurous acid, boil, and pass a current of carbon dioxide through it until the excess of the reagent is completely removed.† Test a drop of the solution with thiocyanate to make sure that the reduction is complete; cool in an atmosphere of carbon dioxide and titrate.

3. *By Metals*

Metallic zinc, cadmium, or aluminum can be used to reduce ferric ions to the ferrous state. This can be done by adding small pieces of the pure metal to the ferric solution in a flask like that shown in Fig. 111 on p. 548 and heating on the water-bath until the ferric solution is reduced and the excess metal all dissolved or removed by rapid filtration through a funnel containing a platinum cone. In carrying out such reductions it must be remembered that titanium, which is likely to be present in small quantities of most rocks, is reduced by these metals to the trivalent condition, whereas it is not reduced by hydrogen sulfide or sulfurous acid. Instead of pure zinc, chemists often prefer to use amalgamated zinc in a so-called *Jones reductor* (Fig. 113). The amalgamated zinc does not react with dilute sulfuric acid and liberate hydrogen but does reduce ferric sulfate solutions because, as the table of reduction potential shows (p. 541) ferric ions are much easier to reduce than are hydrogen ions.

To prepare a Jones reductor, take some 20 to 30 mesh zinc, cover with dilute hydrochloric acid, and add mercuric chloride solution while stirring up the zinc, until the evolution of hydrogen ceases. In the bottom of the reductor tube place a perforated disk or some pieces of glass, on top of this a wad of glass wool, and then just a little asbestos suspension (p. 35). If this asbestos layer is too thick, the reductor is likely to run slowly, and if too thin, some zinc powder may run through and spoil an analysis. Fill the rest of the reductor tube with the well-washed, amalgamated zinc. The use of the reductor is explained below.

* Ferric salts are not completely reduced by sulfurous acid in the presence of considerable hydrochloric or sulfuric acid.

† It is not advisable to depend upon the sense of smell. Test escaping gas from the flask by passing it through dilute sulfuric acid containing a few drops of 0.1 *N* $KMnO_4$ solution. If the latter is not decolorized at the end of 2 or 3 minutes, the excess of sulfurous acid has been removed.

Determination of Iron in Limonite with the Jones Reductor

Weigh out 0.5-g samples to four significant figures and dissolve heating with 20 ml of $6N$ hydrochloric acid. To the resulting fe chloride solution add 12 ml of $18N$ sulfuric acid and evaporat

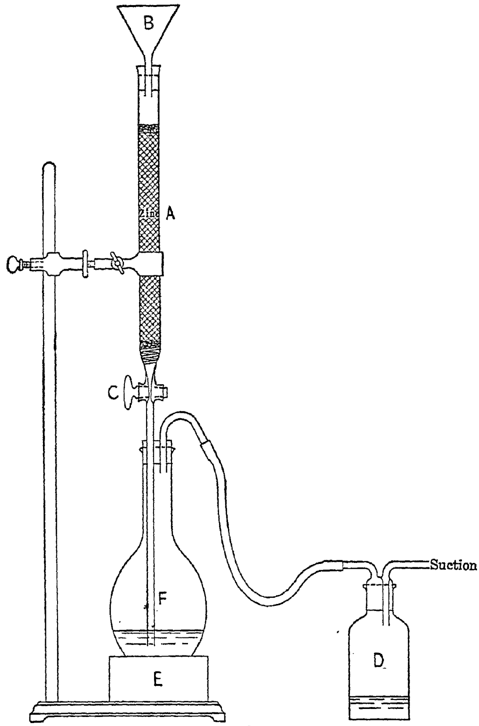

FIG. 113.

boiling, until all hydrochloric acid has been removed, as shown by the lack of odor or by the formation of sulfuric acid fumes. Cool, dilute carefully with 100 ml of water, and run through the properly prepared reductor with which blanks have just been run. From the total volume of permanganate solution used in the analysis, deduct the volume required in the blank.

In making blanks and in all determinations, the procedure is as follows. Add 100 ml of normal sulfuric acid through the funnel, B, with the stopcock C open, using a little suction. When only a little of the dilute acid remains in the funnel, add the solution to be reduced or, in the case of blanks, 50 ml of $1.5N$ sulfuric acid, and when

this has nearly passed out of the funnel, follow with 250 ml of normal sulfuric acid, washing out the original beaker with this acid and adding it in small portions. Finally, pass 100 ml of water through the reductor. At no time, however, should any air be allowed to enter the reductor tube, which should be kept full of water at all times when idle. Run blanks until two successive tests require less than 0.2 ml of 0.1 N permanganate to give a pink color to the acid solution.

4. *By Stannous Chloride*

This method proposed by Zimmermann and Reinhardt* is especially suited for metallurgical purposes, because it can be accomplished most rapidly.

Principle. — The method depends upon the fact that ferric chloride in hot solution is easily reduced by stannous chloride:

$$SnCl_2 + 2\ FeCl_3 + 2\ HCl = H_2SnCl_6 + 2\ FeCl_2$$

The complete decolorization of the solution shows the end point of reduction. The excess of stannous chloride is afterward oxidized by means of mercuric chloride:

$$SnCl_2 + 2\ HgCl_2 + 2\ HCl = H_2SnCl_6 + \mathbf{Hg_2Cl_2}$$

After this treatment, which consumes but a few minutes, manganese sulfate solution is added and the solution is immediately titrated with potassium permanganate, which is added slowly.

Requirements

(*a*) Stannous chloride solution. Dissolve 50 g of stannous chloride in 100 ml of concentrated hydrochloric acid and dilute with water to a volume of 1 l.

(*b*) 6 N hydrochloric acid.

(*c*) Mercuric chloride solution. A saturated solution of the pure commercial salt in water is used.

(*d*) Manganese sulfate solution. See p. 552.

Determination of Iron in Spathic Iron Ore

Procedure. — Weigh out 0.25–0.3 g of the finely powdered mineral into a small beaker, add 20 ml of 6 N hydrochloric acid, cover the beaker with a watch glass, and heat, just below the boiling temperature, until the residue is apparently free from reddish brown mineral. Remove the flame, and add the stannous chloride solution, *drop by drop,* until the iron solution just becomes colorless, avoiding an excess. Cool to at least room temperature and add quickly 10 ml of mercuric chloride solution, whereby a slight silky precipitate of Hg_2Cl_2† is formed. After

* Cf. p. 552.

† If the precipitate produced by mercuric chloride is at all grayish in color, the solution must be thrown away; too large an excess of stannous chloride was used. Moreover, the end point with permanganate is difficult to see if the solution contains much precipitate.

5 minutes, dilute the solution to about 400 ml, add 20–25 ml of the manganese sulfate solution, and titrate the mixture (very slowly) with potassium permanganate until a pink color permanent for 15 seconds is obtained.

(c) Determination of Metallic Iron in the Presence of Iron Oxide

This method is useful for testing *ferrum reductum* which is obtained by the reduction of Fe_2O_3 in a stream of hydrogen. Usually the reduction is not complete and the preparation contains, besides the metallic iron, some oxide, usually assumed to be Fe_3O_4. The value of the preparation depends upon the free iron content.

α. *Method of Wilner*-Merck†*

Principle. — The method is based upon the fact that a neutral solution of mercuric chloride dissolves iron according to the equation

$$\mathbf{Fe} + HgCl_2 = \mathbf{Hg} + FeCl_2$$

while the Fe_3O_4 is not attacked. The solution of ferrous chloride is titrated with permanganate solution.

Procedure. — Place about 0.5 g of *ferrum reductum* powder‡ in a 100-ml graduated flask, from which the air has been replaced by CO_2; add 3 g of solid mercuric chloride and 50 ml of water. Heat the contents of the flask to boiling, by means of a small flame, and boil gently for a minute. Then fill the flask to the mark with boiled water. Cool to 20° and again carefully bring to the mark. Shake well, and allow to stand in the stoppered flask until the precipitate has settled. Pour the liquid through a dry filter, reject the first 15 ml, and catch 20 ml of filtrate in a flask filled with carbon dioxide. To this add 20 ml of 7 *N* sulfuric acid, add 10 ml of manganese sulfate solution,§ dilute to 200 ml, and titrate with 0.1 *N* permanganate solution.

β. *The Ferric Chloride Method*‖

Principle. — A neutral solution of ferric chloride dissolves metallic iron with the formation of ferrous chloride:

$$\mathbf{Fe} + 2\,FeCl_3 = 3\,FeCl_2$$

* *Farm. Tidskrift,* **1880**, 225.

† *Z. anal. Chem.*, **41**, 710 (1902).

‡ A coarse powder is not decomposed quantitatively.

§ See p. 553.

‖ A. Christensen, *Z. anal. Chem.*, **44**, 535 (1905); see also, E. Schmidt, *Chem. Ztg.*, **21**, 700 (1897); A. Marquardt, *Chem. Ztg.*, **25**, 743 (1901); F. Förster and V. Herold, *Z. Elektrochem.*, **16**, 461 (1910).

If the ferrous chloride formed is titrated with permanganate solution, one-third of the iron thus found corresponds to the weight of metallic iron present in the sample.

Proceed in exactly the same manner as in (α) but use 50 ml of ferric chloride solution, obtained by dissolving 2.5 g of anhydrous ferric chloride in cold water, instead of the 3 g of mercuric chloride. Stopper the flask and shake 15 minutes in an atmosphere of CO_2 before diluting to the mark. The ferric chloride should give a clear solution in cold water and be perfectly free from ferrous salt.

2. Determination of Manganese. Method of Volhard*

$$1000 \text{ ml } N \text{ KMnO}_4 \quad \frac{3\text{ Mn}}{10} = 16.48 \text{ g Mn}$$

If an almost boiling, nearly neutral solution of manganese sulfate is slowly treated with a solution of potassium permanganate, each drop will cause the formation of manganous acid (H_2MnO_3). Under ideal conditions the reaction takes place as follows:

$$2\,MnO_4^- + 3\,Mn^{++} + 7\,H_2O \rightarrow 5\,\mathbf{H_2MnO_3} + 4\,H^+$$

According to this equation, 2 $KMnO_4$ (10 equivalents) react with 3 Mn^{++} (cf. p. 545).

A. Guyard, who first determined manganese by this method, assumed that the oxidation took place according to the above equation.

In reality, however, instead of pure manganous acid being precipitated, different acid manganites of varying composition are formed; for example:

$$4\,KMnO_4 + 11\,MnSO_4 + 14\,H_2O = 4\,KHSO_4 + 7\,H_2SO_4 + 5\,\mathbf{Mn(HMnO_3)_2}$$

Volhard has shown that if calcium, barium, or, better still, zinc salts, are present, manganites of these metals are precipitated. The precipitate, although varying in composition, then contains all *the manganese in the quadrivalent form.*

Procedure. — Of manganese ores with 0–20 per cent of manganese take 3 samples of about 1 g each for analysis; use half as much with richer ores. Weigh the samples into a large Erlenmeyer flask (800–1000 ml) and heat with 20 ml of concentrated hydrochloric acid and 3 g of potassium chlorate. After all the liberated chlorine has been evolved, dilute with water to 100 ml.

If a dark residue remains which is likely to contain manganese, rinse into a casserole, evaporate to dryness, and digest the residue for 10 minutes with 10 ml of concentrated hydrochloric acid, warming gently. Dilute with hot water, heat to boiling, and filter back into the Erlenmeyer flask. Ignite the residue in a platinum crucible, fuse with sodium carbonate, extract the melt with dilute hydrochloric acid, evaporate to dryness to render silica insoluble, digest with acid, dilute, and filter into the main solution.

* *Ann. Chem. Pharm.*, **198**, 318 (1879). Cf. W. Fischer, *Z. anal. Chem.*, **48**, 751 (1909); Cahin and Little, *Analyst*, **36**, 52 (1911).

Evaporate the hydrochloric acid solution to a small volume to remove the greater part of the acid, and dilute to 300 ml with cold water in a 500-ml measuring-flask. Add in small portions, while constantly shaking the flask, a suspension of zinc oxide in water until all the iron is precipitated as shown by the sudden coagulation of the precipitate. Shake well and allow the precipitate to settle. If the supernatant solution is colored brownish, add more zinc oxide but avoid the use of too much of the reagent. Dilute to exactly 500 ml, mix thoroughly, filter through a dry filter and take 250 ml for the titration. Dilute with water to about 400 ml, heat to boiling, and add to the first sample 0.1 N permanganate in 5-ml portions until, after shaking and allowing the precipitate to settle, the clear liquid appears pink. This is best observed by holding the flask in an inclined position and looking through the top of the solution against a light background. At first considerable difficulty is caused by the brown color of the suspended manganese precipitate, but after a little practice the operator learns to recognize the end point.

The first titration is rarely correct because it is practically impossible to titrate the first portion within a drop or two of the correct point.

To the second sample, therefore, add nearly as much permanganate at once to the 400 ml of hot solution and continue until the permanganate is no longer decolorized. Cool to about 80°, add 5 ml of 6 N acetic acid, and finish the titration adding 1–2 drops of permanganate at a time. The addition of the acetic acid causes the precipitate to settle and titrating at a temperature below the boiling point gives a more stable end point. Moreover, correct results are obtained with the theoretical factor of the reagent. In the analysis of the third sample add at the start nearly as much permanganate as was used the second time and continue with 0.2-ml additions. Call this last titration the correct one. Allow 0.1 ml of permanganate as a blank and do not attempt to titrate closer than to the nearest 0.1 ml (= 0.2 mg of Mn).

Remarks. — Standardize the permanganate solution under the same conditions against 20 ml of pure manganese sulfate solution (7.550 g $MnSO_4$* per liter) adding 40 ml of 20 per cent zinc sulfate solution, 2 drops of 6 N hydrochloric acid, and diluting to 400 ml. Use 3 samples for the standardization as in the analysis.

Large quantities of iron increase the volume of permanganate used in the titration so that it is best to make up the solution with precipitate to a definite volume and use an aliquot part of the filtered solution. The error produced by the volume of the iron precipitate is not a serious one; although the precipitate appears very bulky, its volume when dry is very small and it is likely to absorb a little manganese. The presence of chromium, cobalt, or vanadium also causes error. If the ore does not contain enough iron to combine with the phosphoric, arsenic, and vanadic acids, and give a fair-sized precipitate with zinc oxide, add 5–10 ml of pure ferric chloride solution, containing 6 g to the liter, before neutralizing.

* Heat the pure, hydrated crystals 1 hour at 400–500° before weighing.

Determination of Manganese in Steel

(a) *Volhard Method*

Weigh out, to three significant figures, three separate portions of 2 g of steel into 300-ml porcelain casseroles. Cover the dishes with watch glasses, and dissolve each sample by the gradual addition of 25 ml of 6 N nitric acid. When the sample has dissolved, raise the cover glass, evaporate to dryness, and ignite carefully to decompose nitrates. Cool and digest the residue with 20 ml of concentrated hydrochloric acid.

If a dark residue remains undissolved, evaporate the solution to dryness again, dehydrate silica by heating an hour at 125°, warm with 10 ml of concentrated hydrochloric acid, dilute, filter, and wash the residue thoroughly, first with a little hot 2 N hydrochloric acid, then with cold water, and finally with hot water. If there is no dark-colored residue containing graphite, this treatment is unnecessary. A carbonaceous residue is always more or less oxidizable and must be removed.

Evaporate the hydrochloric acid to dryness. Moisten the residue with 10 ml of 6 N hydrochloric acid, warm, and evaporate to a small volume but not to dryness. Transfer to a 500-ml measuring-flask, first filtering if there is much residue, and dilute with cold water to about 200 ml. Add 6 N sodium carbonate solution in small portions until the ferric chloride solution has a deep red color and then small quantities of a suspension of zinc oxide in water, shaking after each addition of oxide and continuing until a point is reached where the liquid suddenly coagulates forming a heavy precipitate of ferric hydroxide. Fill the flask with water up to the mark, mix thoroughly by pouring back and forth into a beaker several times, allow the precipitate to settle, and filter through an 18–20 cm filter. Reject the first 5 ml of filtrate and collect the next 250 ml in a measuring-flask. Transfer the solution to a 500-ml flat-bottomed flask, and titrate as described above.

(b) *Bismuthate Method**

1000 ml N $KMnO_4$ = 10.99 g Mn

This method originated with Schneider,† who used bismuth tetroxide as the oxidizing agent; but as the oxide is difficult to prepare free from chlorides, and traces of chloride interfere with the end point of the titration, it was abandoned by Reddrop and Ramage,‡ who proposed the use of sodium bismuthate, $NaBiO_3$. The product sold under this name is of more or less indefinite composition.

The determination is based on the fact that a manganous salt in the presence of nitric acid is oxidized to permanganic acid by sodium bismuthate.

$$2\,Mn^{++} + 5\,NaBiO_3 + 14\,H^+ \rightarrow 2\,MnO_4^- + 5\,Bi^{+++} + 5\,Na^+ + 7\,H_2O$$

* A. A. Blair, *J. Am. Chem. Soc.*, **26**, 793. W. Blum, Reprint No. 186 from *Bull. Bur. Standards*, **8** (1912).

† *Ding. poly. J.*, **269**, 224.

‡ *Trans. Chem. Soc.*, **1895**, 268.

The permanganic acid formed is very stable in a cold solution containing 20–40 per cent of nitric acid. In hot solutions the excess of bismuthate is rapidly decomposed and then the permanganic acid breaks down; as soon as a small amount of manganous salt is formed it reacts with the permanganic acid and manganese dioxide precipitates.

In the cold, however, the excess of the bismuth salt can be filtered off, an excess of ferrous sulfate added to the clear filtrate, and the excess determined by titrating with permanganate. The end point is sharp and the method is extremely accurate except in the presence of cobalt.*

The following conditions are recommended by Blum. To the cold manganous solution containing 20–40 per cent nitric acid (free from nitrous acid) in a volume of 50–150 ml, add a slight excess of bismuthate (usually 0.5–1.0 g), agitate thoroughly for about $\frac{1}{2}$ minute, wash down the sides of the flask with 3 per cent nitric acid,† filter through asbestos, wash with 100 ml of 3 per cent nitric acid, add a slight excess of ferrous sulfate, and titrate at once with permanganate.

Procedure for Steels. — Dissolve 1 g of sample in 50 ml of 4 N nitric acid and boil the solution to expel oxides of nitrogen. Remove from the heat, add about 0.5 g of sodium bismuthate, and boil 2 to 3 minutes. If more than 0.1 per cent manganese is present, a precipitate of manganese dioxide usually appears or, if the manganese content is low, a pink color is produced. If neither a pink color nor a precipitate is produced, add more bismuthate and heat again. Clear the solution by adding a few drops of sulfurous acid, boil 2 to 3 minutes, and cool to 15°. Add 0.5 to 1 g more of bismuthate (enough to leave a *small* excess undissolved), agitate, and allow to stand for 1 minute. Then add 50 ml of 3 per cent nitric acid (3 ml of concentrated HNO_3 + 97 ml of water), and filter through asbestos. A suitable filter can be made by tamping down some glass wool in a funnel and pouring some asbestos fibers suspended in water upon it. If a Gooch crucible is used for filtering, take care that none of the filtrate comes in contact with the rubber that holds the crucible in the filter bottle. A glass filtering crucible can be used. Wash the excess bismuthate with 3 per cent nitric acid until the last runnings are colorless (50 to 100 ml of acid should be used). Add a measured volume of standard ferrous sulfate solution (usually a 25-ml pipetful is sufficient), and titrate the excess with permanganate.‡

The ratio of permanganate to ferrous sulfate solution must be determined daily. Though not strictly necessary, the determination of

* G. E. F. Lundell, *J. Am. Chem. Soc.*, **45**, 2600 (1923).

† One ml of nitric acid, *d.* 1.42, contains nearly 1 g of HNO_3. The solution of 3 ml concentrated nitric acid diluted to 100 ml is approximately a 3 per cent solution both by weight and by volume.

‡ H. F. V. Little, *Analyst*, **37**, 554 (1912) found that it was advisable to filter into a known volume of standardized ferrous solution when the manganese content was high.

this ratio by means of a blank affords a convenient means of testing the efficacy of the filter. The conditions found most satisfactory by Blum are: To 50 ml of nitric acid (25 per cent by volume), add a small amount of bismuthate; shake and allow to stand a few minutes, dilute with 50 ml of 3 per cent nitric acid; filter through the asbestos filter, and wash with 100 ml of 3 per cent nitric acid. To the filtrate, which should be perfectly clear, add a volume of ferrous sulfate approximately equal to that to be used in the subsequent determinations (25 or 50 ml), and titrate at once to the first visible pink. Even for the most accurate work, no end-point correction is required for this titration, provided only that the solutions are always titrated to the same color, and that about the same volumes are used in the standardization and analyses.

The manganese content of the steel can be computed as follows:

Let s = weight of the sample.
A = volume of $KMnO_4$ which is equivalent to the $FeSO_4$ used.
n = volume of $KMnO_4$ used to titrate the excess $FeSO_4$.
N = the normality of the $KMnO_4$ solution.

$$\frac{(A - n)N \times 0.01008 \times 100}{s} = \text{per cent Mn}$$

The following modification of the bismuthate method is useful for rapid work. It depends upon reducing the permanganate formed with a sodium arsenite solution. Sodium arsenite in dilute acid solution is oxidized to arsenate; but under the conditions prevailing in this analysis, the reduction of the permanganate does not take place completely to the manganous condition. With a little practice, however, it is easy to note the point when all the permanganate has been acted upon, and this is taken as the end point although the solution has a greenish tint if much manganese is present.

Rapid Bismuthate Method

Prepare a solution of arsenious acid of which 1 ml = 0.1 mg of Mn by dissolving 0.337 g of pure As_2O_3 and 1.1 g of Na_2CO_3, heating with a little water and finally diluting to exactly 1000 ml in a volumetric flask. Weigh out the As_2O_3 on a watch glass and make sure that the weight does not vary 1 mg from the specified quantity. Test the strength of the solution by measuring out carefully, with a pipet, exactly 2 ml of approximately 0.1 N $KMnO_4$, adding 100 ml of 3 per cent HNO_3 and titrating with the arsenite solution to the disappearance of the purple color.

For the analysis, take exactly 0.1 g of steel (within 1 mg) and proceed precisely as described above but with somewhat less bismuthate. The final volume of the solution after filtering off the excess bismuthate should be about 100 ml. Titrate the solution with the sodium arsenite solution. The volume required divided by 10 should give the percentage of Mn present.

It was originally assumed that the bismuthate method is not well suited for determining large quantities of manganese, but Cunningham and Coltman* have shown how the method can be applied to materials rich in manganese.

Determination of Manganese in an Ore

Treat 2 g of the finely powdered ore with 40 ml of hot 7.5 N nitric acid in a 400 ml covered beaker, adding small portions of hydrogen peroxide from time to time until finally no black residue of pyrolusite is apparent. Rinse off the watch glass and the sides of the beaker and add sodium bismuthate until a permanent precipitate of manganese dioxide results. Boil 2–3 minutes, then add sulfurous acid dropwise until the solution clears and filter. (If the residue is likely to contain manganese, ignite it in a platinum crucible and treat with 1 ml of concentrated sulfuric acid and about 10 ml of hydrofluoric acid. Evaporate under the hood until fumes of sulfuric acid are evolved, cool, dilute with water and add to the main solution; precipitation of barium sulfate will do no harm.) Dilute the solution to exactly 500 ml in a measuring-flask and mix thoroughly by pouring back and forth into a dry beaker.

To determine roughly how much bismuthate will be required, take 25 ml of the solution in a 300 ml Erlenmeyer flask, add 12 ml of concentrated nitric acid (freed from nitrous fumes by bubbling air through the bottle) and about 13 ml of water. Cool, add 1.7 g of sodium bismuthate, agitate for one minute, dilute with 50 ml of water, filter through an asbestos filter and wash the residue with 3 per cent nitric acid. Add 2.5 g of solid ferrous ammonium sulfate and titrate the excess with 0.1 N $KMnO_4$.

For the accurate determination, take 200 ml of the solution in a 750-ml flask, add 50 ml of concentrated nitric acid and 50 ml of water. Cool to room temperature, add all at once 2.6 g of sodium bismuthate for each 0.1 g of manganese present and agitate for one minute. Dilute with 200 ml of water, filter, wash with 3 per cent nitric acid, add sufficient ferrous ammonium sulfate to react with all the manganese (use about 0.75 g for each 0.10 g of manganese) and titrate the excess promptly with permanganate.

(c) *Modified Williams Method*

$$1000 \text{ ml of } N\ KMnO_4 = \frac{Mn}{2} = 27.47 \text{ g Mn}$$

The Williams method depends, in the first place, upon the precipitation of all the manganese as MnO_2 by boiling the manganous solution with concentrated nitric acid and potassium chlorate. The reaction has also been used in qualitative analysis.

$$Mn(NO_3)_2 + 2\,KClO_3 + H_2O \rightarrow MnO_2{\cdot}H_2O + 2\,KNO_3 + 2\,ClO_2\uparrow$$

* *Ind. Eng. Chem.*, **16**, 58–63 (1924). Cf. Little, *loc. cit.*

The precipitate is dissolved in acid and a known quantity of reducing agent, and the excess of the latter is measured by titration with standard potassium permanganate solution. A standard solution of acid ferrous sulfate or ferrous ammonium sulfate is commonly used as the reducing agent, and since such a solution oxidizes slowly on standing in the air it is necessary to determine its strength at least once every day that it is being used.

Julian* used H_2O_2 as the reducing agent and did not bother to filter off the precipitate, but it is unquestionably better to do so because the presence of a little nitrous acid in the solution is likely to cause error in the final titration.

Procedure. — Take 2 to 3 g of steel (weighed to the nearest centigram) in a 500-ml Erlenmeyer flask and dissolve it in 60 ml of 6 *N* HNO_3. When the steel has dissolved, evaporate the solution to sirupy consistency (about 10 ml); add 50 ml of concentrated nitric acid and 3 g of potassium chlorate crystals. Boil the solution on the hot plate for 15 minutes. Then remove the flask from the hot plate, as otherwise the ClO_2 which is liberated on adding chlorate may explode; add 15 ml more of concentrated nitric acid and another 3 g of potassium chlorate. Boil for another 15 minutes. Cool quickly by placing the flask in cold water and rotating the contents. Prepare an asbestos filter by pressing down a little glass wool in a funnel and pouring on it a little asbestos suspension such as is used for Gooch crucibles. Filter through the asbestos, and wash the MnO_2 precipitate with three 10-ml portions of cold water. Transfer the asbestos pad and precipitate back to the original flask. As solvent, prepare a mixture of 900 ml water, 43 ml of 3 per cent hydrogen peroxide, 25 ml of phosphoric acid, *d.* 1.70, and preserve it in a glass-stoppered bottle. Of this well-mixed solution take out 25-ml portions by means of a pipet. Usually one portion of the solution is sufficient to dissolve the MnO_2 precipitate and leave an excess of H_2O_2. At the same time, take two separate portions of the solution for direct titration with permanganate. In every case, dilute with water to about 200 ml and titrate with standard potassium permanganate. In using the pipet make sure that it has been cleaned recently with cleaning solution so that it will drain well and that it has been rinsed out with three small portions of the solution which is to be measured. Make sure that the pipet is filled from the bottom up to the mark on the stem, and, after allowing the contents to drain out, touch the tip of the pipet to the side of the beaker just above the solution. When used in this way pipets are more accurate than the ordinary buret.

The reactions that take place with the hydrogen peroxide are these:

$$H_2O_2 + \mathbf{MnO_2} + 2\,H^+ \rightarrow Mn^{++} + 2\,H_2O + O_2\uparrow$$
$$5\,H_2O_2 + 2\,MnO_4^- + 6\,H^+ \rightarrow 2\,Mn^{++} + 8\,H_2O + 5\,O_2\uparrow$$

* *J. Am. Chem. Soc.*, **15**, 113 (1893); cf. *J. Anal. Chem.*, **2**, 249 (1888).

If, in the analysis of s grams of steel, 25 ml of H_2O_2 were used which were equivalent, as found by direct titration, to A milliliters of $KMnO_4$ and the excess H_2O_2 reacted with n milliliters of $KMnO_4$ which was N-normal, then

$$\frac{(A - n)N \times 0.02747}{s} \times 100 = \text{per cent Mn}$$

(d) *Persulfate Method**

In a hot solution of a manganous salt containing silver nitrate as catalyzer, ammonium persulfate causes the formation of permanganic acid.

$$2\,Mn^{++} + 5\,S_2O_8^{--} + (Ag^+) + 8\,H_2O \rightarrow 2\,MnO_4^- + 10\,SO_4^{--} + (Ag^+) + 16\,H^+$$

Without the silver salt, manganous acid, H_2MnO_3, is precipitated. In the routine analysis of steel it is customary to discharge the permanganate color by adding standard sodium arsenite. Under the conditions that usually prevail, the arsenic is completely oxidized to the quinquevalent condition; the manganese of the permanganate is not reduced to colorless manganous salt but to a green solution which contains manganese partly trivalent and partly quinquevalent. The arsenite solution, therefore, must be standardized in exactly the same way it is used in the analysis against permanganate solution or by means of a Bureau of Standards steel.

Dissolving Solution. — Mix together 5 ml of 0.1 N $AgNO_3$, 40 ml of water, 2 ml of concentrated H_2SO_4, and 15 ml of concentrated HNO_3.

Titrating Solution. — Dissolve exactly 0.337 g of pure As_2O_3 and about 1.1 g of Na_2CO_3 in about 60 ml of hot water. When the solids have all dissolved completely, transfer to a liter measuring-flask and make up to exactly 1 l. One milliliter = 0.1 mg Mn. Test the strength of the solution by taking a measured volume of 0.1 N $KMnO_4$ (2.00 ml is suitable), reducing it with a little H_2SO_3, and then proceeding exactly as in the analysis of steel, using the same quantities of reagents.

Procedure. — Weigh out portions of exactly 0.100 g (within 1 mg) into 250-ml Erlenmeyer flasks, and heat each portion with 15 ml of the dissolving solution until all the steel has dissolved and the red nitrous fumes have been expelled. Remove from the hot plate; add 100 ml of hot water and 10 ml of 10 per cent $(NH_4)_2S_2O_8$ solution. Heat to boiling, and maintain this temperature for 30 seconds. Remove from the hot plate and cool under running water to about 15°. (If necessary use ice-water.) Titrate the cold solution until the permanganate color is discharged. Pay no attention to a return of the color on standing.

The persulfate, in the presence of silver cations, slowly oxidizes the manganous ions to permanganate, but this reaction is so slow in the cold that there is no serious error if the titration takes place fairly quickly. If the cold solution is treated with just

* Walters, *Proc. Eng. Soc. Western Pa.*, **17**, 257 (1901); *Chem. News*, **84**, 239, H. P. Smith, *Chem. News*, **90**, 237 (1904). Rubricus, *Chem. Ztg. Repert.*, **1905**, 247. F. Kunze, *Chem. Ztg.*, **29**, 1017 (1905). H. Marshall, *Z. anal. Chem.*, **43**, 418; 655 (1904).

sufficient NaCl solution to precipitate the silver before the titration, the end point lasts much better; but if the solution is hot when the chloride is added, some permanganate is likely to be reduced. The above very rapid method has never been regarded as suitable for umpire analysis, but students usually obtain excellent results agreeing within 0.02 per cent, or less, of the weight of sample. If considerable manganese is present the solution is yellow or green at the end point, but the practiced eye can easily tell when all the permanganate color is gone.

3. Determination of Uranium. Method of Belohoubek,* Zimmermann,† Hillebrand‡

$$1000 \text{ ml } N \text{ KMnO}_4 = \frac{\text{U}}{2} = 119.1 \text{ g U}$$

This method is especially suited for testing the purity of a precipitate of U_3O_8 obtained in the analysis of uranium minerals. It is based upon the fact that when U_3O_8 is heated in a closed tube with dilute sulfuric acid at 150°–175° it is readily decomposed according to the equation

$$U_3O_8 + 4\ H_2SO_4 = 2\ UO_2SO_4 + U(SO_4)_2 + 4\ H_2O$$

forming uranyl and uranous sulfates. The latter compound is oxidized to the former by means of potassium permanganate:

$$2\ KMnO_4 + 5\ U(SO_4)_2 + 2\ H_2O = 2\ KHSO_4 + 2\ MnSO_4 + H_2SO_4 + 5\ UO_2SO_4$$

If it is desired to express the results in terms of the original U_3O_8, of which two-thirds is not oxidized by the permanganate, then 1 ml N $KMnO_4 = \frac{U_3O_8}{2000} = 0.4218$ g U_3O_8.

Procedure. — Place 1 g of U_3O_8 in a tube closed at one end, add 10–15 ml of 5 N sulfuric acid and make the open end of the tube narrower by heating in a blast lamp and drawing it out somewhat. Remove the air in the tube by inserting a long capillary so that it reaches to the bottom of the tube containing the substance and conducting a current of carbon dioxide through it; finally seal the larger tube without removing the capillary. Heat the tube in a "bomb furnace" at 150–175° until everything has dissolved to a clear green liquid. After cooling, open the tube by making a scratch with a file and touching it with a hot glass rod. Pour the contents into a large porcelain dish, dilute with distilled water to 500–700 ml, and titrate with 0.1 N $KMnO_4$ solution until a permanent pink color is obtained.

Remark. — In quantitative analysis uranium is often precipitated as ammonium uranate by ammonium hydroxide (see p. 112), and the uranate dissolves in acids forming uranyl, UO_2^{++} salts. It is possible to reduce the 6-valent uranium of the uranyl salt to 4-valent uranous salt, and uranium, like iron, titanium, and molybdenum, can be determined volumetrically by reducing in a Jones reductor and titrat-

* *J. prakt. Chem.*, **99**, 231.
† *Ann. Chem. Pharm.*, **232**, 285.
‡ *U. S. Geol. Survey*, Bull. 78.

ing with permanganate.* Unfortunately, the oxidation and reduction of the uranium do not always proceed quantitatively in the desired manner. If the solution is passed quickly through the reductor the results are different from those obtained when the solution is added slowly, but in the latter case some of the uranium is reduced too far and it is necessary to allow the air to act upon the reduced solution in order to get the uranium into the quadrivalent condition. Atmospheric oxidation, however, may cause oxidation of uranium to uranyl salt. Jander and Reeh† claim to have overcome these difficulties by using as reducing agent a piece of aluminum such as was used in 1922 as a German coin. Their procedure is as follows:

Make a perforated glass basket of 10–15 ml capacity from a small test-tube. Bend a stout piece of pure sheet aluminum to fit the basket and attach the basket by platinum wire to a glass rod long enough to reach to the bottom of a 400-ml Erlenmeyer flask. Insert the rod in a two-holed rubber stopper which is also provided with a Bunsen valve (see p. 548). Place 100 ml of uranyl solution, containing not more than 0.2 g of uranium, in the 400-ml flask, add 20 ml of concentrated sulfuric acid, and heat to boiling. Remove the flame and insert the stopper carrying the Bunsen valve and the rod with the basket and aluminum in place. Allow the reduction to take place out of contact with air for an hour:

$$3\,UO_2^{++} + 2\,Al + 12\,H^+ \rightarrow 3\,U^{++++} + 2\,Al^{+++} + 6\,H_2O$$

Raise the stopper and add a little sodium bicarbonate solution, to fill the flask with carbon dioxide. With a stream of water from a wash bottle, rinse off the rod, the glass basket, and the excess aluminum, and titrate with 0.1 N KMnC

$$5\,U^{++++} + 2\,MnO_4^- + 2\,H_2O \rightarrow 5\,UO_2^{++} + 2\,Mn^{++} + 4\,H^+$$

4. Determination of Oxalic Acid

1000 ml N $KMnO_4$ $\qquad$ 63.02 g $H_2C_2O_4 \cdot 2H_2O$

The procedure is exactly the same as was described under the standardization of permanganate by means of sodium oxalate (p. 546).

5. Determination of Calcium

$$1000 \text{ ml } N\, KMnO_4 = \frac{Ca}{2} = 20.04 \text{ g Ca}$$

Precipitate the calcium as described on p. 85 in the form of its oxalate, filter, and wash with hot water. Transfer the moist precipitate to a beaker by means of a stream of water from the wash-bottle, and dissolve the precipitate remaining on the filter, allowing hot 2 N sulfuric acid to pass through it several times. To the turbid solution in the beaker, add 20 ml of 18 N sulfuric acid, dilute with hot water to a volume of 300–400 ml, and titrate the oxalic acid with 0.1 N $KMnO_4$ solution.

* O. S. Pulman, Jr., *Am. J. Sci.* [4] **16**, 229.

† *Z. anorg. allgem. Chem.* **129**, 293–301 (1923).

6. Determination of PbO_2 in Minium [Red Lead, Pb

Method of Lux*

$$1000 \text{ ml } N \text{ } KMnO_4 = \frac{PbO_2}{2} = 119.6 \text{ g } PbO_2 = 342.8 \text{ g } Pb_3O_4$$

Principle. — If lead peroxide (PbO_2) is treated with oxalic acid or sodium oxalate in acid solution, the oxalate ion is oxidized according to the following equation:

$$PbO_2 + C_2O_4^{=} + 4\,H^+ \rightarrow Pb^{++} + 2\,CO_2 + 2\,H_2O$$

If the decomposition takes place with a measured amount of titrated oxalic acid solution and the excess of the latter is titrated by means of potassium permanganate solution, the difference shows the amount of oxalic acid necessary to effect the reduction of the lead peroxide.

Procedure. — Weigh out about 0.25 g of minium (red lead) into a porcelain dish and heat with 20–30 ml of 2 N nitric acid. The original oxide is thereby changed into soluble lead nitrate and brown, insoluble H_2PbO_3:

$$\mathbf{Pb_3O_4} + 4\,HNO_3 = 2\,Pb(NO_3)_2 + H_2O + \mathbf{H_2PbO_3}$$

After the sample is dissolved, add 50 ml of 0.2 N oxalic acid, heat the solution to boiling, and titrate hot with 0.2 N $KMnO_4$. If t milliliters of 0.2 N $KMnO_4$ solution were used, then $50 - t$ milliliters of 0.2 N $H_2C_2O_4$ were necessary for the reduction of the amount of PbO_2 contained in the minium (a grams) taken for analysis. There is present, therefore,

$$\frac{(50 - t) \times 2.392}{} \text{ per cent } PbO_2 \text{ or } \frac{(50 - t) \times 6.856}{} = \text{per cent } Pb_3O_4$$

The Diehl-Topf iodometric method to be described later has been adopted by the American Society of Testing Materials for the analysis of red lead.

7. Determination of MnO_2 in Pyrolusite

$$1000 \text{ ml } N \text{ } KMnO_4 = \frac{MnO_2}{2} = 43.47 \text{ g M}$$

(a) *Method of Levol and Poggiale, Modified by G. Lunge*†

After drying at 120° to constant weight, place 1.087 g of the finely powdered pyrolusite in a 250-ml flask which is provided with a Contat valve (see p. 548). Expel the air by conducting CO_2 into the flask, and then add 75 ml of the ferrous sulfate solution, prepared as described below, close the flask, and heat its contents over a small flame

* *Z. anal. Chem.*, **19**, 153.

† *Chem. techn. Untersuchungsmethoden.*

until there is no longer any dark-colored residue. Cool quickly, dilute with 200 ml of water, and titrate the excess of ferrous sulfate with 0.5 N $KMnO_4$ solution. Immediately before the analysis, determine the titer of the ferrous sulfate solution by taking 25 ml of it, diluting to 200 ml, and titrating with permanganate.

By the treatment of the pyrolusite with ferrous sulfate, the following reaction takes place:

$$\mathbf{MnO_2} + 2\,FeSO_4 + 2\,H_2SO_4 = Fe_2(SO_4)_3 + MnSO_4 + 2\,H_2O$$

The computation of the percentage of MnO_2 is as follows:

75 ml $FeSO_4$ solution..............	require	T milliliters 0.5 N $KMnO_4$
75 ml $FeSO_4$ + 1.087 g pyrolusite...	"	t milliliters 0.5 N $KMnO_4$

∴ 1.087 g pyrolusite are equivalent to $T - t$ milliliters 0.5 N $KMnO_4$

corresponding to $(T - t) \times 0.02173$ g MnO_2 and in percentage

$$\frac{(T - t) \times 0.02173 \times 100}{1.087} = 2\,(T - t) \text{ per cent } MnO_2$$

Prepare the ferrous sulfate solution as follows: slowly pour 200 ml of concentrated sulfuric acid, with stirring, into 500 ml of water, and while the mixture is still hot add 100 g of powdered $FeSO_4 \cdot 7H_2O$ crystals; on stirring, the salt should dissolve within a few minutes. Dilute the solution to 1 l. When cold it is ready for use.

(*b*) *Method of Fresenius-Will, Modified by Mohr*

$$\mathbf{MnO_2} + C_2O_4^{--} + 4\,H^+ \rightarrow Mn^{++} + 2\,CO_2 + 2\,H_2O$$

For each analysis, weigh out portions of the finely ground ore, which has been dried to constant weight at 120°, into 300-ml Erlenmeyer flasks, using samples that do not vary more than 0.05 g from 0.45 g. Add to each portion of ore a carefully weighed portion of pure sodium oxalate, using at least one and one-half times as much oxalate as pyrolusite but not more than 0.8 g in any case. Add 50 ml of water and 50 ml of 6 N sulfuric acid and heat, without boiling hard, until no more pyrolusite remains undissolved. Keep the flasks covered with watch glasses, and do not allow the solutions to evaporate to below 85 ml, adding hot water from time to time if necessary. When all the black ore has dissolved, dilute to 200 ml and titrate with 0.1 N permanganate, keeping the solution above 60°.

If s is the weight of pyrolusite used, r the weight of sodium oxalate,

and n the milliliters of N normal permanganate required for the excess oxalate,

$$\left(\frac{r}{0.067 \times N} - n\right)\frac{N \times 0.0435 \times 100}{} \qquad \text{of}$$

In this equation, 0.067 is the equivalent weight of sodium oxalate and 0.0435 the equivalent weight of manganese dioxide.

8. Determination of Formic Acid

(a) *Method of Lieben**

$$1000 \text{ ml } N \text{ } KMnO_4 = \frac{3 \times HCOOH}{10} \qquad 13.80 \text{ g } HCOOH\dagger$$

In cold *acid* solutions permanganate reacts very slowly with formic acid, and in a hot solution the latter is lost by volatilization, so that the titration in open vessels is impossible; in *alkaline* solutions, on the other hand, the oxidation takes place readily and quantitatively in the cold:

$$2\ KMnO_4 + 3\ HCO_2K = 2\ K_2CO_3 + KHCO_3 + 2\ MnO_2 + H_2O$$

In this reaction the permanganate is reduced only to the quadrivalent condition so that it has only three-fifths of its oxidizing power as determined in the standardization. Hence the weight of formic acid equivalent to 1 ml of N permanganate (normal against sodium oxalate) is $\frac{3}{5} \times HCO_2H$

Procedure. — Neutralize the formic acid by an excess of sodium carbonate, and allow permanganate to run into the hot sodium formate solution until the clear liquid above the precipitate is colored pink (cf. p. 558).

(b) *Method of H. C. Jones*‡

$$1000 \text{ ml } N \text{ } KMnO_4 = HCO_2H \qquad 23.01 \text{ g formic acid}$$

Add an excess of permanganate to the alkaline solution of the formate, heat 5–10 minutes on the water-bath, make acid with 6 N sulfuric acid, add an excess of 0.1 N oxalic acid solution, and titrate the excess of oxalic acid with permanganate at 70°.

If T = total volume of 0.1 N permanganate used and t the volume of 0.1 N oxalic acid then

$$(T - t)\ 0.002301 = \text{weight of formic acid}$$

* *Monatsh.*, **14**, 746, and **16**, 219.

† Ber., **10**, 1075 (1877).

‡ *Am. Chem. J.*, **17**, 539.

(c) *Method of Blackadder**

Proceed exactly as in (*b*) but after heating on the water-bath, add 2–3 g of potassium iodide, neutralize with $6\,N$ hydrochloric acid, add 15 ml in excess, and titrate the liberated iodine with $0.1\,N$ thiosulfate. If T is the volume of $0.1\,N$ permanganate used and t the volume of $0.1\,N$ thiosulfate, the computation is the same as under (*b*).

9. Analysis of Nitrous Acid (Lunge)†

$$1000 \text{ ml } N\ KMnO_4 = \frac{HNO_2}{2} = \frac{47.018}{2} = 23.51 \text{ g } HNO_2$$

On account of the volatility of nitrous acid, measure out the aqueous solution of the nitrite, or the solution of nitrous acid in concentrated sulfuric acid (nitrose), from a buret into 400 ml of $0.75\,N$ sulfuric acid containing a known volume of permanganate solution, warmed to 40°. Have the tip of the buret dipping below the surface of the acid permanganate solution, and stir constantly. The nitrous acid is thereby oxidized to nitric acid:

$$2\,KMnO_4 + 5\,HNO_2 + 3\,H_2SO_4 = K_2SO_4 + 2\,MnSO_4 + 3\,H_2O + 5\,HNO_3$$

and the decolorization of the solution shows the end point. Toward the end the nitrous acid must be added slowly, for the change from red to colorless requires some time.

10. Analysis of Hydrogen Peroxide

$$1000 \text{ ml } N\ KMnO_4 = \frac{H_2O_2}{2} = 17.01 \text{ g } H_2O_2$$

Place 10 ml of commercial 3 per cent hydrogen peroxide in a 100-ml measuring-flask, dilute to the mark with water, and, after thoroughly mixing, transfer 10 ml (= 1 ml of the original solution) to a beaker, and dilute with water to a volume of 300–400 ml. After adding 20–30 ml $7.5\,N$ sulfuric acid, titrate the solution with $0.1\,N$ $KMnO_4$ until a permanent pink color is obtained. The following reaction takes place:

$$2\,KMnO_4 + 5\,H_2O_2 + 4\,H_2SO_4 = 2\,KHSO_4 + 2\,MnSO_4 + 8\,H_2O + 5\,O_2$$

Frequently it happens that the first drop of the permanganate causes a permanent coloration of the solution. This shows that either not enough sulfuric acid is present, or else there is no more hydrogen peroxide left in the solution. In this case add a little more sulfuric acid,

* *Dissertation*, Zürich, 1911.

† *Ber.*, **10**, 1075 (1877).

when if the coloration still remains the preparation is surely spoiled, as can be shown by the titanic or chromic acid tests (cf. Vol. I).

The amount of hydrogen peroxide is expressed either as percentage by weight or as percentage by volume.

Example. — 10 ml of the above-mentioned dilute solution of hydrogen peroxide (= 1 ml of the original solution) required 17.86 ml of 0.1 N $KMnO_4$ solution, corresponding to $17.86 \times 0.001701 = 0.03038$ g H_2O_2. As the specific gravity of the original hydrogen peroxide solution can be assumed to be 1, it therefore contains 3.04 per cent H_2O_2.

When expressed in "percentage by volume" the result shows how many cubic centimeters of oxygen can be obtained from 100 ml of the solution.

In this case 100 ml of the hydrogen peroxide solution contain 3.04 g of H_2O_2 and, on being decomposed, 2 moles of H_2O_2 sets free 1 mole of O_2.

$$2\ H_2O_2 = 2\ H_2O + O_2$$

or 22.39 l of oxygen at 0° C and 760 mm pressure; consequently 3.04 g H_2O_2 will evolve $x = \frac{3.04 \times 11200}{34.02} = 1000$ ml oxygen measured under standard conditions of temperature and pressure.

One hundred milliliters of the commercial hydrogen peroxide, therefore, will evolve 1000 ml of oxygen, *i.e.*, 10 times its own volume. This is sometimes designated as 10 volume hydrogen peroxide.

Other methods for determining hydrogen peroxide will be given later. (See Index.)

11. Analysis of Barium Peroxide

$$1000 \text{ ml } N\ KMnO_4 \quad \frac{BaO_2}{2} \quad 84.685 \text{ g } BaO_2$$

Weigh 0.2 g of the substance into a 400-ml beaker, cover with 300 ml of cold water, and add with constant stirring, 20–30 ml of 2 N hydrochloric acid. When all the BaO_2 has dissolved, titrate the solution with 0.1 N $KMnO_4$. The addition of H_2SO_4 is not advisable, as the precipitated $BaSO_4$ is likely to enclose some BaO_2 which will then escape the titration.

Another method for the analysis of BaO_2 has been proposed by Kassner.*

12. Analysis of Potassium Percarbonate

$$1000 \text{ ml } N\ KMnO_4 = K_2C_2O_6 = 99.10 \text{ g } K_2C_2O_6$$

Weigh 0.25 g of potassium percarbonate into 300 ml of cold, N sulfuric acid, in which it dissolves with vigorous evolution of carbon dioxide and formation of an equivalent amount of hydrogen peroxide:

$$K_2C_2O_6 + 2\ H_2SO_4 = 2\ KHSO_4 + 2\ CO_2 + H_2O_2$$

Titrate the latter with 0.1 N potassium permanganate.

* *Arch. Pharm.*, **228**, 432.

13. Analysis of Persulfates (Persulfuric Acid,)

$$1000 \text{ ml } N \text{ KMnO}_4 = \begin{cases} 97.07 \text{ g } H_2S_2O_8 \\ 114.1 \text{ g } (NH_4)_2S_2O_8 \\ 135.2 \text{ g } K_2S_2O_8 \end{cases}$$

A solution of persulfuric acid does not reduce permanganate, nor does it react with titanic acid; on the other hand it oxidizes ferrous salts immediately in the cold to ferric salts, and by means of this behavior it can be easily determined. The ammonium and potassium salts are now commercial products, and are analyzed as follows: Weigh 0.3 g of the salt into a flask fitted with a Bunsen valve, replace the air by carbon dioxide, add 30 ml of a freshly titrated solution of ferrous sulfate and then 200 ml of hot water. Close the flask and rotate its contents. The salt dissolves without difficulty, and the ferrous sulfate is oxidized:

$$H_2S_2O_8 + 2\ FeSO_4 = Fe_2(SO_4)_3 + H_2SO_4$$

After all the salt has dissolved, cool the contents of the flask by placing the flask in cold water, and titrate the excess of ferrous salt with 0.1 N $KMnO_4$.

The ferrous sulfate must be added to the persulfate, and then the hot water. If the hot water is added first, the persulfate is decomposed somewhat and the results obtained will be low. In this way it is found that:

30 ml ferrous sulfate solution require T milliliters 0.1 N $KMnO_4$ solution.

30 ml ferrous sulfate + a grams persulfate require t milliliters 0.1 N $KMnO_4$ solution.

Consequently a grams of persulfate correspond to $(T - t)$ milliliters 0.1 N $KMnO_4$.

In the case of the potassium salt, since 1000 ml N $KMnO_4$ = 135.2 g $K_2S_2O_8$, and 1 ml 0.1 N $KMnO_4$ = 0.01352 g $K_2S_2O_8$, we have: $(T - t) \times 0.01352$ g $K_2S_2O_8$ in a grams of the commercial salt, or in percentage: $\frac{1.352\,(T - t)}{a}$ = per cent $K_2S_2O_8$. With the ammonium salt the factor becomes 0.01141 instead of 0.01352.

The ferrous sulfate necessary for this determination is prepared as described on p. 568.

Persulfates may also be analyzed very satisfactorily by means of oxalic acid.* When a sulfuric acid solution of a persulfate is treated with oxalic acid alone, there is no perceptible reaction. On adding a small amount of silver sulfate as catalyzer, however, a lively evolution of carbon dioxide takes place, and at the water-bath temperature the reaction is soon completed.

$$H_2S_2O_8 + H_2C_2O_4 = 2\ H_2SO_4 + 2\ CO_2$$

The excess of the oxalic acid can be titrated with permanganate.

Procedure. — Place 0.5 g of the persulfate in a 400-ml Erlenmeyer flask; add 50 ml of 0.1 N oxalic acid solution and 0.2 g of silver sulfate dissolved in 20 ml of 10 per cent sulfuric acid. Heat the mixture on the water-bath until the evolution of carbon dioxide ceases; this requires not more than 15 or 20 minutes. Dilute the solution to about 100 ml with water at about 40° and titrate with 0.1 N permanganate.

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* R. Kempf, *Ber.*, **38**, 3965 (1905).

14. Determination of Hydroxylamine (Raschig)*

$$1000 \text{ ml } N \text{ KMnO}_4 \quad 2 \quad 16.52 \text{ g } NH_2OH$$

Principle. — Hydroxylamine is oxidized in hot acid solution by means of ferric salts to form nitrous oxide and an equivalent amount of ferrous salt:

$$2\ NH_2OH + 4\ Fe^{+++} \rightarrow 4\ Fe^{++} + N_2O + 4\ H^+ + H_2O$$

The quantity of ferrous salt is determined by titration with 0.1 N potassium permanganate.

Procedure. — Place 0.1 g of the hydroxylamine salt in a 500-ml flask and dissolve in a little water. Add 30 ml of a cold, saturated solution of ferric-ammonium alum and 10 ml of 7.5 N sulfuric acid. Heat the contents of the flask to boiling and keep at this temperature for 5 minutes. Then dilute the solution with distilled water to a volume of about 300 ml and immediately titrate with permanganate solution.

Remark. — If only slightly more than the theoretical amount of the ferric salt is added, the oxidation of the hydroxylamine does not take place entirely in accordance with the above equation, but part of the substance is oxidized to nitric oxide:

$$2\ NH_2OH + 6\ Fe^{+++} \rightarrow 6\ Fe^{++} + 2\ NO + 6\ H^+$$

and it is then impossible to obtain exact results.

15. Determination of Ferrocyanic Acid (de Haën)†

$$1000 \text{ ml } N \text{ KMnO}_4 = 1 \text{ mole } K_4Fe(CN)_6 = 368.3 \text{ g } K_4Fe(CN)_6$$

Principle. — By oxidation in acid solution, ferricyanic acid is formed from ferrocyanic acid:

$$5\ H_4Fe(CN)_6 + MnO_4^- + 3\ H^+ \rightarrow 5\ H_3Fe(CN)_6 + Mn^{++} + 4\ H_2O$$

Good results are obtained only when the solution is dilute and contains considerable acid. If too much ferrocyanide is present, a precipitate of $K_2Mn[Fe(CN)_6]_2$ is likely to form. In this case it is necessary to make sure that sufficient acid is present and to dilute the solution. The end point is a change from greenish yellow to yellowish pink.

Procedure. — Dissolve 10 g of potassium salt in 1 l of water. Mix and transfer 50 ml to a white porcelain dish. Add 100–150 ml of water and 10–20 ml of 7.5 N sulfuric acid and titrate with 0.1 N permanganate.

16. Determination of Ferricyanic Acid

$$1000 \text{ ml } N \text{ KMnO}_4 = 1 \text{ mole } K_3Fe(CN)_6 = 329.2 \text{ g } K_3Fe(CN)_3$$

Principle. — The potassium ferricyanide is reduced in alkaline solution to potassium ferrocyanide, which is titrated with permanganate.

* *Ann. Chem. Pharm.*, **241**, 318.

† *Ibid.*, **90**, 160.

Procedure. — In a 300-ml measuring-flask dissolve 6.0 g of the ferricyanide in water, make the solution alkaline with potassium hydroxide, heat to boiling, and add an excess of a concentrated ferrous sulfate solution. At first brown ferric hydroxide is precipitated, later black ferrous-ferric hydroxide is formed, and this shows the completion of the reaction. Cool, dilute the contents of the flask with water to the mark, filter through a dry filter (after mixing), reject the first runnings, and take 50 ml of the filtrate (= 1 g of the substance) for the titration with 0.1 N $KMnO_4$ solution.

17. Determination of Chloric Acid

$$1000 \text{ ml } N \text{ } KMnO_4 = \frac{RClO_3}{6} = \begin{cases} 20.43 \text{ g } KClO_3 \\ 17.74 \text{ g } NaClO_3 \end{cases}$$

Dissolve 5 g of potassium chlorate, or 4 g of the sodium salt, in water, and dilute the solution to 1 l. After thoroughly mixing, transfer 10 ml to a flask fitted with a Bunsen valve and expel the air from the flask by a current of carbon dioxide. After this add 50 ml of a freshly standardized 0.1 N solution of ferrous sulfate in 2.5 N H_2SO_4 and boil the solution 5 minutes. The following reaction takes place:

$$KClO_3 + 6\, FeSO_4 + 3\, H_2SO_4 = KCl + 3\, Fe_2(SO_4)_3 + 3\, H_2O$$

After cooling, dilute the solution with cold distilled water to 200 ml, add 10 ml of manganous sulfate solution (cf. p. 552), and titrate the excess of the ferrous sulfate with potassium permanganate.

If 50 ml ferrous sulfate .... required T milliliters 0.1 N $KMnO_4$ sol.
and 50 ml " " + 10 ml chlorate sol. " t milliliters 0.1 N " "
then 10 ml of chlorate solution = 0.01a grams = $(T - t)$ milliliters 0.1 N $KMnO_4$ "
where a = original weight of the sample

The substance contains $\dfrac{20.43 \times (T - t)}{a}$ per cent of $KClO_3$

18. Determination of Nitric Acid (Pelouze-Fresenius)

$$1000 \text{ ml } N \text{ } KMnO_4 = \frac{RNO_3}{3} \begin{cases} 21.01 \text{ g } HNO_3 \\ 28.34 \text{ g } NaNO_3 \\ 33.71 \text{ g } KNO_3 \end{cases}$$

This method depends upon the fact that on heating a nitrate with an acid ferrous chloride solution the nitric acid is reduced to nitric oxide:

$$2\, KNO_3 + 6\, FeCl_2 + 8\, HCl = 2\, KCl + 2\, NO + 4\, H_2O + 6\, FeCl_3$$

As a measure for the amount of nitrate reduced we have:

(1) The excess of ferrous salt. (2) The ferric salt produced. (3) The nitric oxide formed.

The method of Schlösing-Grandeau described on p. 403 is based upon the measurement of the nitric oxide formed. C. D. Braun* estimates the amount of ferric salt

* *J. prakt. Chem.*, **81**, 421 (1860).

formed, while Pelouze and Fresenius determine the amount of ferrous salt not used up in the reduction of the nitric acid.

Procedure. — Place 1.5 g of pure iron wire in a long-necked flask, and expel the air by passing a current of pure carbon dioxide through it for 2–3 minutes. Then add 30–40 ml of concentrated hydrochloric acid, place the flask in an inclined position, and close by means of a rubber stopper through which tubes pass so that a current of carbon dioxide can be introduced. Heat the solution on the water-bath in this atmosphere of carbon dioxide until the iron has completely dissolved, and allow the solution to cool in a current of the gas. Meanwhile weigh 0.25–0.3 g of the nitrate into a small glass tube closed at one end. Drop this into the acid solution of the ferrous sulfate and quickly close the flask again. Heat as before for 15 minutes, while continuing the stream of carbon dioxide. Have the exit tube through from the flask dipping into a beaker filled with water so that there is no chance of any air getting back into the flask. Finally heat the solution to boiling and keep hot there until the dark color disappears and the yellow color of the ferric chloride becomes apparent. To make sure that the nitric oxide is entirely removed boil 5 minutes longer and then allow to cool in the atmosphere of carbon dioxide. When cold pour the solution into a beaker, rinse the flask with a little boiled water, and dilute to about 400 ml. Add 10 ml of manganese sulfate solution (p. 552), and titrate the unoxidized ferrous salt with 0.5 N $KMnO_4$ solution.

Determine the purity of the iron wire by titrating 1 g of the wire after similar treatment with acid and manganese sulfate solution.

If a grams of potassium nitrate and p grams of the wire were taken for the analysis, t milliliters of 0.5 $KMnO_4$ were required to oxidize the excess of iron, and p grams of the wire require T milliliters of 0.5 $KMnO_4$, then:

$$\frac{(T - t) \times 1.685}{a} = \text{per cent } KNO_3$$

Remark. — This method gives results just as accurate as those obtained by the method of Devarda (p. 402), which is much easier to carry out.

19. Determination of Vanadic Acid

$$1000 \text{ ml of } 0.1\,N\ KMnO_4 = \frac{V_2O_5}{20} = 9.096 \text{ g } V_2O_5$$

Conduct sulfur dioxide into the boiling acid solution of an alkali vanadate until the solution is clear blue in color; by this means the

vanadic acid is reduced to vanadyl salt:

$$2\,H_3VO_4 + H_2SO_3 + H_2SO_4 \rightarrow V_2O_2(SO_4)_2 + 5\,H_2O$$

$$5\,V_2O_2^{++++} + 2\,MnO_4^- + 22\,H_2O \rightarrow 10\,H_3VO_4 + 2\,Mn^{++} + 14\,H^+$$

Continue boiling and introduce a current of carbon dioxide through the solution until the escaping gas will no longer decolorize a solution of potassium permanganate, showing that the excess of the sulfur dioxide has been expelled. Titrate the hot solution with potassium permanganate until a permanent pink color is obtained. The end point is easily recognized only when the solution is hot. This accurate determination is used for the analysis of vanadium in iron and steel, or in ores. (Cf. pp. 295, 580.)

20. Blair Method for Determining Phosphorus in Steel*

$$1000 \text{ ml of } 0.1\,N\ KMnO_4 = \frac{P}{360} = 0.0862 \text{ g P}$$

Transfer the yellow precipitate, obtained as described on p. 529 to a paper filter but use for washing the precipitate an acid ammonium sulfate solution (1 l of water, 25 ml concentrated H_2SO_4, and 15 ml strong ammonia). Wash the precipitate promptly with ten 5-ml portions of this acid sulfate solution, wetting the upper edge of the filter paper each time and allowing each portion to drain through the filter paper before adding the next.

Dissolve the ammonium phosphomolybdate precipitate in 25 ml of $3\,N$ ammonium hydroxide, wash the filter with hot water, and treat the filtrate with 10 ml of concentrated sulfuric acid. It is now ready for reduction with the Jones reductor (see p. 554). Run a blank with the reductor before each series of determinations, and whenever the reductor has stood idle for 3 hours. After a reductor has stood over night, it should be well washed with dilute sulfuric acid, before even running a blank test.

In making blanks and in all determinations, the procedure is as follows. Add 100 ml of normal sulfuric acid through the funnel, *B*, with the stopcock *C* open, using a little suction. When only a little of the dilute acid remains in the funnel, add the solution to be reduced or, in the case of blanks, 50 ml of $1.5\,N$ sulfuric acid, and when this has nearly passed out of the funnel, follow with 250 ml of normal sulfuric acid, washing out the original beaker with this acid and adding it in small portions. Finally, pass 100 ml of water through the reductor and titrate with permanganate. Air should not be allowed to enter the

* Andrew Blair, *The Chemical Analysis of Iron.*

reductor tube, which should be kept full of water at all times when idle. Run blanks until two successive tests require less than 0.2 ml of 0.1 N permanganate to give a pink color to the acid solution.

In the original method, the reduced solution was caught in an empty flask and it was assumed that the MoO_3 of the phosphomolybdate precipitate is reduced to $Mo_{24}O_{37}$; 1 ml of 0.1 N $KMnO_4$ = 0.0000886 g P. The molybdenum is reduced completely to the trivalent condition by the amalgamated zinc:

$$(NH_4)_3PO_4 \cdot 12MoO_3 + 23\ NH_4OH = 12\ (NH_4)_2MoO_4 + (NH_4)_2HPO_4 + 11\ H_2O$$
$$2\ MoO_4^{--} + 3\ Zn + 16\ H^+ \rightarrow 2\ Mo^{+++} + 3\ Zn^{++} + 8\ H_2O$$

The trivalent molybdenum is slowly oxidized by the air in the flask and by that shaken into the solution during the titration. A practiced manipulator usually titrates so that about 3 per cent of the total oxidation is accomplished by the air, and this corresponds to the assumption that Blair made with respect to the formation of the hypothetical $Mo_{24}O_{37}$. The only safe way to avoid this error is to catch the reduced solution, before it comes in contact with air, in 50 ml of 10 per cent ferric alum solution (100 g of ferric alum, 25 ml of concentrated sulfuric acid, and 40 ml of sirupy phosphoric acid per liter).

This ferric alum solution does not change the reduced molybdenum entirely back to the 6-valent condition but it does oxidize it sufficiently to prevent the effect of the atmosphere, and for every equivalent of molybdenum oxidized an equivalent of reduced iron is formed so that the solution titrates exactly as if a perfect reduction was obtained without the use of the ferric salt. Since the precipitate contains 1 P:12 Mo, and the valence change of the Mo is 3, it is clear how the normal weight is computed. When this ferric alum solution is used in the analysis, it must be present also in running the blanks.

To illustrate the computation assume that the ammonium phosphomolybdate precipitate from 2 g of steel required by the above method 12 ml of 0.1 *N* permanganate solution. The blank on the reductor and ferric alum was 0.18 ml. The phosphorus present in the steel is then: $(12 - 0.18) \times 0.00431$ per cent.

If 2.16 g of steel is taken for analysis, the percentage of phosphorus will be 0.004 times the net volume of 0.1 *N* permanganate in milliliters when ferric alum is used.

21. Chromium in Steel

Chromium, when present as trivalent chromic cations, is very similar to ferric iron with respect to its behavior toward many reagents. Practically all methods for determining chromium in iron and steel are based upon its oxidation to the valence of 6 as chromic acid, dichromate, or chromate. Small quantities of chromium can be determined colorimetrically, but quantities larger than a few hundredths of 1 per cent are usually determined by adding a measured volume of reducing agent, usually acid ferrous sulfate solution, and titrating the excess with potassium permanganate solution. A great many different methods have been proposed for carrying out the oxidation.

(a) *The Barba Method* *

Principle. — The steel is dissolved in dilute sulfuric acid, the iron is oxidized to the ferric state by means of nitric acid, and the chromium is oxidized by the addition

* *J. Iron and Steel Institute,* **1893**, ii, 536; *Iron Age,* **52**, 153.

of strong permanganate solution. The excess of the latter is destroyed by boiling in ammoniacal solution, the solution is acidified again, the precipitated manganese dioxide filtered off, a known volume of standard ferrous sulfate solution is added to an aliquot part of the filtrate, and the excess of the latter is titrated with permanganate.

Procedure. — Dissolve exactly 1.25 g of steel in 20 ml of $6\,N$ sulfuric acid, and when the sample has dissolved, add concentrated nitric acid, drop by drop, until all the iron is oxidized to the ferric state. Boil the solution to remove nitrous fumes, dilute to 150 ml, add 5 ml of 6 per cent potassium permanganate solution and boil briskly for 15–20 minutes. Remove from the hot plate, wash the sides of the beaker with water and pour 25 ml of concentrated ammonium hydroxide down the sides of the beaker. Stir the liquid vigorously and place on the cooler part of the hot plate, for if it is heated too rapidly there is likely to be loss by "bumping." Digest with occasional stirring for 15 minutes, or until the permanganate is all decomposed as shown by the disappearance of the pink color. Then carefully add 20 ml of $16\,N$ sulfuric acid and heat the solution to boiling. Transfer to a 250-ml measuring-flask, cool to room temperature, and dilute to the mark. After thoroughly mixing by pouring back and forth several times into a dry beaker, filter the solution and use exactly 200 ml (1 g of metal) for the rest of the analysis. Add 50 ml of standard ferrous sulfate solution (see p. 587), and titrate the excess with $0.1\,N$ permanganate.

Computation. — When the ferrous sulfate solution is added, the chromium is reduced from chromic acid to chromic salt in accordance with the following equation:

$$2\,H_2CrO_4 + 6\,FeSO_4 + 6\,H_2SO_4 = Cr_2(SO_4)_3 + 3\,Fe_2(SO_4)_3 + 8\,H_2O$$

The ferrous sulfate solution is not very stable and should be titrated against the permanganate at the same time the analysis is made. If 50 ml of the ferrous sulfate solution are equivalent to T_1 milliliters of N-normal permanganate, and T_2 milliliters of permanganate were used in titrating the excess of ferrous sulfate in the analysis of s grams of steel, then

$$\frac{-\,T_2) \times N \times 1.734}{} = \text{per cent Cr}$$

(*b*) *Sodium Bismuthate Method*

1000 ml of $0.1\,N$ $KMnO_4$ = 1.734 g Cr

Principle. — Sodium bismuthate, $NaBiO_3$, is often used for oxidizing manganese from the bivalent to septavalent condition (cf. p. 559). This oxidation takes place best in a *cold* solution containing 20–40 per cent of nitric acid (free from nitrous acid) in a volume of 50–100 ml.* Moreover, an excess of sodium bismuthate should be

* William Blum, *J. Am. Chem. Soc.*, **34**, 1395.

present and the solution must not stand long. Under these conditions scarcely any chromium is oxidized so that the manganese may be determined by the bismuthate method even when chromium is present.* If the solution is heated to boiling, the permanganate is decomposed and the manganese is precipitated as manganese dioxide. Chromium, on the other hand, is oxidized in *hot* solutions from the trivalent to the sexavalent condition, and the chromic acid is not decomposed by boiling unless some reducing agent is present. In hot solutions, therefore, it is possible to oxidize the chromium by sodium bismuthate, to filter off the precipitated manganese dioxide, and to determine the chromium in the filtrate by adding a known volume of standard ferrous sulfate solution and titrating the excess as in (*a*).

Procedure. — Dissolve 2 g of steel in a 250-ml Erlenmeyer flask in 50 ml of 4 *N* nitric acid. If there is any carbonaceous residue, as in the analysis of cast irons, it must be removed and should be filtered off and examined for chromium by fusion with an alkaline oxidizing flux. If the metal is difficultly soluble in nitric acid, it is sometimes necessary to add sulfuric acid to hasten the solution.

When the sample is entirely dissolved, cool the solution to between 65° and 75° and add 2 g of sodium bismuthate. Agitate the contents of the flask for a few minutes, and then wash down the sides of the flask with a little water. Heat the solution and gently boil until all the permanganate formed from the manganese in the steel is decomposed as shown by the color. This usually requires about 15 minutes. Add 50 ml of 0.5 *N* nitric acid, and filter off any precipitated manganese dioxide or undissolved sodium bismuthate on an asbestos filter. Wash the residue 3 times with 50-ml portions of the dilute nitric acid. Cool to room temperature by running tap water over the flask and finally dilute with distilled water to 500 ml. Add a measured volume of ferrous sulfate solution and titrate the excess with permanganate as in (*a*).

* This statement has been made by several writers, but considerable evidence has accumulated to prove that, as ordinarily carried out in the laboratory, the bismuthate method for the determination of manganese in a steel containing chromium is likely to give high results owing to a partial oxidation of chromium by the bismuthate. If the essential conditions with regard to temperature, acidity, and time allowed for the completion of the reaction are adjusted very carefully it is probably possible to get accurate results in the manganese determination, but in ordinary practice it is advisable to separate the manganese and chromium by precipitating the latter. This can be accomplished satisfactorily by means of zinc oxide (cf. Volhard method, p. 558). The manganese can then be determined by the bismuthate method in an aliquot part of the filtrate.

Determination of Chromium and Vanadium in Alloy Steel *

In this procedure the manganese, chromium, and vanadium are first obtained in the bivalent, trivalent and quadrivalent states respectively by dissolving in acid. By the action of persulfate in the presence of silver salt as catalyzer, the bivalent manganese is oxidized to the valence of 7, the trivalent chromium to the valence of 6, and the quadrivalent vanadium to the valence of 5. By the addition of a limited quantity of chloride, the permanganic acid is reduced to manganous salt and the excess persulfate is removed by boiling. The chromic acid is then reduced to chromic salt by a measured quantity of ferrous solution, and the excess titrated with permanganate. The chromium content corresponds to the amount of ferrous salt required. The vanadium, to be sure, is reduced to vanadyl salt by the ferrous iron but is again oxidized to vanadic acid by the permanganate so that it affects the analysis only by making the end point a slow one.

After the titration, all manganese is present as manganous salt, all chromium as chromic salt, and all vanadium as vanadate. Another portion of ferrous salt serves to reduce the vanadium to quadrivalent vanadyl salt. The excess ferrous iron can be oxidized by stirring with persulfate solution without oxidizing the vanadium and the vanadyl salt can be titrated with permanganate.

Procedure. — Weigh out 2 g of sample, or less if more than 2 per cent of chromium is present, into a 600-ml beaker, and cover it with a mixture of 45 ml water, 12 ml concentrated sulfuric acid, and 6 ml of phosphoric acid, *d.* 1.7. Heat until there is no further action, add 5 ml of concentrated nitric acid, and boil to decompose carbides and oxidize the iron. (If a yellow residue of tungstic acid is formed, filter it off and reject it. If a black carbide residue remains, filter, ignite, fuse with sodium carbonate, and add the aqueous extract of the melt to the main solution.) Dilute to about 300 ml; add 10 ml of 0.1 N silver nitrate and 15 ml of freshly prepared 8 per cent ammonium persulfate solution. If a permanganate color does not develop from the manganese in the steel, add more silver nitrate and more persulfate. Then boil 8 minutes to decompose the excess persulfate, add 2 ml of 6 N hydrochloric acid, and heat 10 minutes after the permanganate color, or any precipitated manganese dioxide, has disappeared. Cool, dilute to 400 ml, add 25 ml of 0.1 N ferrous ammonium sulfate solution from a pipet, and test a drop of the solution on a white background with a freshly prepared solution of potassium ferricyanide. If the blue test is not obtained, add another portion of ferrous salt. Titrate the excess with 0.1 N permanganate until the pink end point persists after stirring for 1 minute.

In this analysis a perceptible excess of permanganate is required because of the dilution and the color of the chromic salt. To allow for

* Procedure based on Methods of the Chemists of the United States Steel Corporation. Students making the analysis for the first time find it easier to follow these directions than those of the preceding method.

this error, assume that the milli-equivalent of chromium is 0.01744 instead of the theoretical value. The end point is a little difficult because of the slow rate of oxidation of the vanadium in cold, dilute solutions.

Determination of Vanadium. — After the chromium determination, add 5 ml of standard ferrous ammonium sulfate solution from a pipet. Stir and test a drop of the solution for ferrous iron with fresh ferricyanide solution, adding another pipetful of ferrous salt if necessary. Add 8 ml of 15 per cent ammonium persulfate solution and stir 1 minute to oxidize the excess of ferrous salt. Then titrate with permanganate till the end point persists after 1 minute's stirring. In this case, the vanadium is titrated directly and 1 ml of 0.1 N permanganate oxidizes 0.005096 g of vanadium. The error due to dilution and color of the chromic ions is positive. From the percentage of vanadium found, subtract 0.02 plus 0.018 times the percentage of chromium in the sample.

The important chemical reactions involved in the persulfate method for determining chromium and vanadium in steel can be expressed by the following equations:

Oxidation with persulfate in the presence of Ag^+ ions:

$$2\,Cr^{+++} + 3\,S_2O_8^{--} + 7\,H_2O \rightarrow Cr_2O_7^{--} + 6\,SO_4^{--} + 14\,H^+$$
$$2\,VO^{++} + S_2O_8^{--} + 4\,H_2O \rightarrow 2\,HVO_3 + 2\,SO_4^{--} + 6\,H^+$$
$$2\,Mn^{++} + 5\,S_2O_8^{--} + 8\,H_2O \rightarrow 2\,HMnO_4 + 10\,SO_4^{--} + 14\,H^+$$

Removal of the catalyzer and reduction o

$$Ag^+ + Cl \quad \rightarrow AgCl$$
$$2\,HMnO_4 + 14\,H^+ + 10\,Cl \quad \rightarrow 2\,Mn^{++} + 8\,H_2O + 5\,Cl_2$$

Reduction with

$$+ 6\,Fe^{++} + 14\,H^+ \qquad + 6\,Fe^{+++} + 7\,H_2O$$
$$HVO_3 + Fe^{++} + 3\,H^+ \qquad Fe^{+++} + 2\,H_2O$$

Titration with $KMnO_4$:

$$5\,Fe^{++} + MnO_4^- + 8\,H^+ \rightarrow 5\,Fe^{+++} + Mn \qquad 4\,H_2O$$
$$+ 6\,H_2O \rightarrow 5\,HVO_3 \qquad + 7\,H^+$$

Reduction with $FeSO_4$ the second time:

$$HVO_3 + Fe^{++} + 3\,H^+ \rightarrow VO^{++} \qquad 2\,H_2O$$

Removal of excess $FeSO_4$ the second time:

$$2\,Fe^{++} + S_2O_8^{--} \rightarrow 2$$

Final titration:

$$5\,VO^{++} + MnO_4^- + 6\,H_2O \rightarrow 5\,HVO_3 + Mn^{++} + 7\,H^+$$

22. Determination of Molybdenum in Wulfenite and Molybdenite*

1. *Method of Dissolving Wulfenite*

Dissolve 1 g of the powdered ore by treatment with 15 ml of concentrated nitric acid and 7 ml of concentrated sulfuric acid in a 150-ml covered beaker at a temperature just short of boiling. When practically complete decomposition has been effected, evaporate until fumes of sulfur trioxide are expelled freely. Cool, add 40 ml of water, boil to dissolve the bulk of the molybdenum, cool to tap-water temperature, and filter into a 150-ml beaker; the residue consists of lead sulfate, silica, and possibly small amounts of undecomposed ore, and tungstic and molybdic acids. Save both the residue and the filtrate.

Dissolve the lead sulfate in hot ammonium acetate solution (see p. 187), washing until the ammonium acetate filtrate gives no test for lead with ammonium sulfide solution. Ignite the silicious residue in a platinum crucible and remove silica by treating it with sulfuric and hydrofluoric acids. Evaporate till all the excess acid is expelled. If an appreciable residue remains after this treatment, fuse it with potassium pyrosulfate and test for molybdenum by means of tartaric acid and ammonium sulfide as further described. The residue, however, seldom contains any molybdenum.

2. *Method of Dissolving Molybdenite*

Treat 0.5–5 g of the finely pulverized sample with 10–35 ml of concentrated nitric acid and 7–10 ml of concentrated sulfuric acid in a 250-ml beaker, covered with a watch glass. Digest at a temperature somewhat below the boiling point until most of the molybdenite appears to have been decomposed, and then evaporate until strong fumes of sulfur trioxide are evolved. When the beaker and its contents have cooled, add 50 ml of water and boil briskly for a few minutes. Filter into a 150-ml beaker. Wash the residue with hot water, then 6 or 8 times with 4 *N* ammonium hydroxide, and finally with hot water, allowing the washings to run into the main filtrate.

Treat the silicious residue (which will also contain nearly all lead and barium present in the ore) with ammonium acetate solution (cf. p. 187) and ignite the remainder at a very low red heat in a porcelain crucible, cool, transfer to a platinum crucible, treat with 2 or 3 drops of concentrated sulfuric acid and several milliliters of hydrofluoric acid, and evaporate until sulfuric acid has been completely expelled. Fuse the

* Method furnished by the Bureau of Standards and based upon the work of J. A. Holliday and A. M. Smoot.

small residue remaining with sodium carbonate, extract with water, and add the water extract to the main solution.

3. *Method of Analysis*

To the solution containing all of the molybdenum, add sufficient ferric sulfate to provide 10 times as much iron as there is arsenic present; from 0.3 to 0.4 g is usually ample. Nearly neutralize the acid with ammonia (do not add enough to impart a red tint to the solution), heat nearly to boiling and pour slowly and with vigorous stirring into 75 ml of nearly boiling $9N$ ammonium hydroxide contained in a 250-ml beaker. When the precipitate has settled, filter and wash thoroughly with hot water. Dissolve the precipitate in a slight excess of hot $7.5N$ sulfuric acid, heat to boiling, and pour again into 75 ml of boiling $9N$ ammonium hydroxide. Collect the two filtrates, containing all the molybdenum, in a 500-ml beaker. It is essential that arsenic, which is usually present in these ores, be eliminated, and the method described furnishes a simple and effective way for accomplishing this. The addition of ferric sulfate should be omitted only if arsenic is known to be absent.

To the combined ammoniacal filtrates, add 3 g of tartaric acid, and when the acid has dissolved, saturate the warm solution with hydrogen sulfide. The presence of tartaric acid is necessary to prevent the subsequent precipitation of vanadium and tungsten sulfides. If these elements are known to be absent its use may be dispensed with. Under these conditions the molybdenum remains in solution as ammonium thiomolybdate, $(NH_4)_2MoS_4$, which imparts a deep red color to the solution. If a small precipitate of insoluble sulfides separates out, filter and wash with hydrogen sulfide water. Make the thiomolybdate solution *slightly acid* with sulfuric acid (cf. p. 274).

Heat for a short time, allow the precipitate to settle, filter, and wash thoroughly with hydrogen sulfide water containing a little of sulfuric and tartaric acids.

The filtrate from the molybdenum sulfide sometimes contains appreciable amounts of molybdenum.

Boil off the hydrogen sulfide, add an excess of bromine water to oxidize molybdenum, expel the excess by boiling, make ammoniacal as before and treat with hydrogen sulfide and acid as outlined on p. 274. If any more molybdenum sulfide is formed, recover it.

Place the molybdenum sulfide precipitate and filter paper in a 250-ml flask and treat with 6 ml of concentrated sulfuric acid and 10 ml of concentrated nitric acid. Evaporate to fumes and repeat the nitric acid treatment, evaporating until the filter paper has been completely

destroyed and every trace of yellow color due to carbonaceous matter has disappeared. When this has been accomplished, allow the solution to fume strongly for a short while, cool, add 5 ml of water, and again evaporate to fumes to insure the expulsion of every trace of nitric acid. Cool, add 75 ml of water and boil for a few minutes, which should give a perfectly clear solution. Add 5 g of pure, shot zinc (0.002 per cent iron or under) and boil the solution until most of the zinc has dissolved; this results in partial reduction of the molybdenum and complete precipitation of the traces of copper which are usually present. Filter on an asbestos or "alundum" filter to remove the undissolved zinc and the copper.

Reduce the molybdenum completely as described on p. 576 and titrate with $0.1\,N$ permanganate; 1 ml $0.1\,N$ permanganate solution = 0.003200 g of molybdenum.

23. Determination of Titanium*

1000 ml $0.1\,N$ $KMnO_4$ = 0.1 gram-atom Ti = 4.790 g Ti

Principle. — The reduction of titanium from the quadrivalent to trivalent condition proceeds rapidly and quantitatively in 1.1 to $1.8\,N$ H_2SO_4 solution by passage through a Jones reductor. Organic compounds, nitric acid, tin, arsenic, antimony, molybdenum, iron, chromium, vanadium, tungsten, uranium, and columbium must be absent but, with the exception of the rare element columbium, all these can be easily separated from titanium. Nitric acid can be removed by repeated evaporation with sulfuric acid. Arsenic, antimony, and tin can be removed as sulfides from a solution sufficiently acid to prevent hydrolysis of the titanium. Iron can be precipitated as sulfide from an alkaline tartrate solution (see p. 114), and the organic matter then removed by treatment with nitric and sulfuric acids. Chromium, vanadium, tungsten, and uranium can be removed by oxidation in alkaline solution with sodium peroxide and boiling to precipitate titanium hydroxide.

Procedure. — Carry out the reduction as described on p. 576 for molybdenum taking the precaution to wash out the reductor with dilute sulfuric acid before each run which is carried out in the following order: 25 to 50 ml of $1.1–1.8\,N$ sulfuric acid, 150 ml of the same strength acid containing 0.12 g of titanium or less, 100 ml more of acid, and finally 100 ml of water. Catch the solution in 3 times the theoretical quantity of ferric sulfate dissolved in $3\,N$ sulfuric acid, and titrate the ferrous sulfate solution with permanganate. The reduction takes place at any temperature between 25° and 100°, and it is not necessary to expel air from the solutions used in the reductor.

$$+ Zn \rightarrow 2\,Ti^{+++} + Zn^{++}$$
$$Fe^{+++} \rightarrow Fe^{++} + '$$

* G. E. F. Lundell and H. B. Knowles, *J. Am. Chem. Soc.*, **45**, 2620 (1923).

Rapid Determination of Titanium in Ores

The following method of analysis has proved useful for the rapid evaluation of ore samples which are practically free from the interfering elements enumerated above. The entire analysis can be made in less than an hour and the results agree satisfactorily.

Weigh out 0.5 g of 200-mesh ore into a clean, dry, 8-inch test-tube together with about 7 g of fused potassium bisulfate. Tap the sides of the tube to drive down adhering particles, and clamp the tube loosely in such a way that it can be readily swung in a horizontal plane.

Heat the mass gently until the flux has melted and the greater part of the water has been expelled from the flux. When an orange coloration is noticeable along the sides of the tube at the top of the melt, raise the temperature gradually to redness and fuse until there are no more bubbles arising from the bottom and no white particles in the upper portion. Then heat any portion of the tube where there is any evidence of spattering. Next swing the tube about and allow the molten mass to run half way up the tube. In a few minutes the mass will solidify and the melt will crack so that it can be easily dislodged from the tube with the aid of a steel spatula.

Add to the tube 30 ml of 18 N sulfuric acid and heat until the melt has dissolved to a clear solution. Disregard a slight turbidity. An insoluble residue is usually silica or a difficultly soluble sulfate. If TiO_2 forms at this stage by hydrolysis, it can be distinguished on account of its relatively high index of refraction and appears as sharply contrasted white lumps. These may be dissolved by heating 10 minutes with 5–10 ml more of the 18 N acid.

Dilute the solution to 250 ml and pass through a Jones reductor as described on p. 576 but using very little if any suction, and having a lump of marble, weighing about 5 g, in the flask to provide an atmosphere of carbon dioxide, and with no ferric sulfate in the flask. First pass 50 ml of 3–5 per cent sulfuric acid through the cleaned reductor tube (cf. p. 584), then the titanium solution, next 100 ml more of 3–5 per cent acid, and finally 100 ml of water. Add 5 ml of concentrated potassium thiocyanate solution and titrate the reduced titanium with standard ferric alum solution* until a light orange or red color is permanent for 90 seconds. As long as the solution shows a violet color due to trivalent titanium, add the ferric alum solution fairly rapidly in 5-ml portions, shaking as little as possible. Run a blank to determine how much ferric alum is required to give an end point in 500 ml of 3 per cent sulfuric acid, using the same volume of indicator as used in the

* 50 g $Fe_2(SO_4)_3 \cdot (NH_4)_2SO_4 \cdot 24H_2O$ dissolved in 1 l of 0.5 N H_2SO_4.

analysis. Standardize the ferric alum solution against 0.2 g of pure TiO_2 fused and treated as in the analysis.

B. Potassium Dichromate Methods

1. Determination of Iron according to the Method of Penny

1000 ml N $K_2Cr_2O_7$ = 1 gram-atom Fe = 55.84 g Fe

Potassium dichromate is one of the well-known oxidizing agents used in volumetric analysis. It reacts, for example, with ferrous, stannous, or titanous salts and is reduced, thereby, to trivalent chromic salt. Equations for the reduction of the dichromate ion and oxidation of ferrous ion, etc., have been given on p. 476. Expressed in terms of electrons, ϵ, the equation for the reduction of dichromate can be written

$$Cr_2O_7^{--} + 14\,H^+ + 6\,\epsilon = 2\,Cr^{+++} + 7\,H_2O$$

and that of the oxidation of ferrous ion

$$Fe^{++} - \epsilon = Fe^{+++}$$

These equations represent what actually takes place when the reduction of the dichromate is accomplished at the cathode and the oxidation of the iron is brought about at the anode of an electrolytic cell. There are 6.06×10^{23} actual atoms of iron in a gram-atom and if we multiply the actual charge of the electron by 6.06×10^{23} we obtain the value 96,500 coulombs which is called a faraday. When 6 faradays of electricity pass through an electrolytic cell containing an acid solution of dichromate at the cathode and a ferrous salt at the anode, 1 mole of dichromate will be reduced and 6 moles of ferrous iron will be oxidized. The above equations, therefore, show that the equivalent weight of dichromate is one-sixth of its molecular weight and of ferrous ion it is one atomic weight. The equation

$$Cr_2O_7^{--} + 6\,Fe^{++} + 14\,H^+ \rightarrow 2\,Cr^{+++} + 6\,Fe^{+++} + 7\,H_2O$$

is one representing six equivalent weights of both dichromate and iron. The equation, of course, could be written with one equivalent weight of oxidizer and reducer

$$\tfrac{1}{6}\,Cr_2O_7 + Fe^{++} + 2\tfrac{1}{3}\,H^+ \rightarrow \tfrac{1}{3}\,Cr^{+++} + Fe^{+++} + 1\tfrac{1}{6}\,H_2O$$

but it is better not to use fractional parts of molecules in equations.

Preparation and Standardization of Dichromate Solution

Prepare an approximately tenth-normal solution of potassium dichromate by dissolving not more than 5 g of the salt in water and diluting the solution to the volume of about 1 l.

Prepare an approximately tenth-normal solution of ferrous ammonium sulfate by mixing 40 g of the crystals with 50 ml of 6 N sulfuric acid and diluting to about 1 l. The ferrous ions in this solution oxidize slowly from atmospheric oxygen that dissolves in the solution. The acid is necessary, therefore, to keep the salt in solution since the original salt contains acid combined with bivalent ferrous ions and not enough for the trivalent iron formed by oxidation. The strength of this solution will diminish slowly from day to day. The dichromate solution, on the other hand, is very stable.

To determine the relative strengths of the two solutions, fill a glass-stoppered buret with the dichromate solution, taking the usual precautions with respect to cleaning and rinsing, and fill a plain buret with the ferrous solution. Or, since the relative strengths of the two solutions change slightly from day to day and the determination may have to be repeated frequently, it is somewhat more convenient to use a 25-ml pipet for the ferrous solution, cleaning the pipet carefully (see p. 467) and rinsing it with three portions of the solution.

Run out from the buret about 40 ml of the ferrous solution into a beaker or flask of about 300-ml capacity. Add 10 ml of 6 N hydrochloric acid and 100 ml of water. Mix and titrate with the potassium dichromate solution.

Determination of the End Point. — The end point of this titration can be determined in three ways: (1) by means of an external indicator, (2) by an internal indicator, and (3) by the potentiometer.

(1) The end point of the titration of ferrous ions with dichromate can be determined by taking a drop of the solution and testing it on a white porcelain "spot plate" with a drop of potassium ferricyanide solution. This method is capable of giving excellent results after a little practice. Objections can be raised that some of the solution is lost by taking out the drops of solution for the tests, and if the testing is started too soon, the loss may be appreciable. Since a drop of 0.05 ml is only 1/4000 of a total volume of 200 ml, this error is not serious if the iron content is less than 0.1 g when the first test is made. Another difficulty lies in the fact that a negative test for Fe^{++} in a single drop of solution does not prove positively that the entire solution contains less than 0.2 mg of Fe^{++} unless the test serves to indicate 0.00005 mg of Fe^{++} in the drop taken.

(2) Just as there are dyestuffs which change color at a definite p_H value of an aqueous solution and serve as indicators in alkalimetry and acidimetry, so there are certain organic substances which change color as a result of oxidation or reduction. Diphenylamine, $(C_6H_4)_2NH$, diphenylbenzidine $(-C_6H_4 \cdot NH \cdot C_6H_5)_2$, and diphenylamine sulfonic acid, $(C_6H_4)NH(C_6H_3 \cdot SO_3H)$, are such substances. Each of these substances is oxidized less readily than ferrous ions. During the oxidation of Fe^{++} by $Cr_2O_7^{--}$, the Fe^{++}/Fe^{+++} potential falls as the concentration of Fe^{++} becomes smaller and that of the Fe^{+++} becomes larger, or, in other words, it becomes harder for the oxidation to take place. There is not quite enough difference between the oxidation-reduction potentials of the Fe^{++}/Fe^{+++} and that of the above-mentioned

organic substances to make sure that the oxidation of the Fe^{++} is complete before that of the amine starts, but this difficulty as well as the effect of yellow ferric chloride in the solution can be overcome by adding some phosphoric acid which removes Fe^{+++} and $FeCl_3$ from the solution, forming a colorless acid phosphate complex. On the other hand, it requires a measurable quantity of the dichromate solution to accomplish the oxidation of the organic compound. This causes a slight error in the opposite direction.

(3) Since the oxidation-reduction potential shown by a platinum electrode measured against a standard calomel cell changes sharply as soon as 1 drop of 0.1 *N* dichromate solution in excess is added, the potentiometer is capable of indicating a sharp end point in the titration of a ferrous solution with dichromate. This method will not be explained here.

It is important to use the same method in standardizing the solution as in the analysis because a slight excess of reagent causes a low standardization value and a high value in an analysis. A titration error, therefore, is compensated when the same error is made in the standardization and in the analysis. The compensation is exact when the same volume of reagent is used in the analysis as in the standardization.

Method 1. Prepare a fresh solution of about 10 mg of pure potassium ferricyanide in 10 ml of distilled water. Do not attempt to use a solution that was prepared on another day. With a stirring-rod, transfer small drops of this indicator solution to the cavities in a spot plate or to a paraffin coating on a white surface. When about 30 ml of the dichromate solution have been added from a buret, take out a drop of the solution on the end of a stirring-rod and add it to a drop of the potassium ferricyanide solution. Wash the stirring-rod before returning it to the solution. If the test shows an intense blue color, continue adding the dichromate in 1.0 to 0.25 ml portions until only a light blue test is obtained, and then test after each drop or two.

If the indicator solution has stood for some time and a little ferrocyanide is present, a good end point will not be obtained. If the indicator solution is too strong or more than a small drop is used, the test will appear green instead of blue owing to the yellow color of the reagent; and with a strong indicator solution a reddish appearance is sometimes obtained. It is best to add a series of small drops of indicator solution to the test plate and add the drops of titrated solution in regular sequence, noting the buret reading corresponding to each test made near the end point. Take as end point the first test in which a blue does not develop within 1 minute.

Compute the value of 1 ml of ferrous solution in terms of the dichromate solution by dividing the volume of dichromate solution required by the volume of ferrous solution taken.

Method 2. To a carefully measured volume (30–40 ml) of the ferrous solution add 5 ml of phosphoric acid, *d.* 1.7, and 0.3 ml of 0.01 *M* solution of the sodium salt of diphenylamine sulfonic acid, and dilute to about 400 ml.

To prepare the indicator solution, dissolve 0.32 g of the barium salt of diphenylamine sulfonic acid in 100 ml of water, add 0.5 g of sodium sulfate, mix, and allow the barium sulfate precipitate to settle. Decant off the clear solution. If this indicator is not available, a solution of 0.2 g diphenylamine in 100 ml of pure, concentrated sulfuric acid can be used instead.

Add the dichromate solution slowly while stirring until the pure green color changes to a gray, a greenish gray, or a bluish green if considerable iron is present. From this point, add the dichromate 1 drop at a time until the first tinge of purple appears and remains on stirring. From the total volume of dichromate used, subtract 0.05 ml as a blank on the indicator. Divide the volume of dichromate required by the volume of ferrous solution taken to get the value of 1 ml of the latter in terms of the former.

Standardization of the Dichromate Solution. — Potassium dichromate can be obtained sufficiently pure to serve as a standard. A solution of potassium dichromate of known strength, therefore, can be obtained by weighing out the requisite quantity of the pure, recrystallized salt (4.904 g for 1 l of tenth-normal solution) into a volumetric flask, dissolving in a little water, diluting up to the mark, and mixing thoroughly by pouring back and forth at least four times into a beaker which is clean and dry at the start. The solution can be standardized in three ways: (1) against a sample of pure ferrous ammonium sulfate, (2) against a sample of pure iron wire or iron of known purity, or (3) against a ferrous solution which has been titrated within a few hours against a solution of potassium permanganate which has been standardized recently against sodium oxalate. If the first method is chosen, it is always well to test the solution after it has been prepared by one of the other methods.

Against the second method of standardization, objection has been raised that it has been found difficult to prepare absolutely pure iron. Moreover, the impurity present may be oxidizable so that if the purity of the sample is known it is also desirable to know what the impurities are. Electrolytic iron, therefore, has been recommended, but even this is sometimes impure and it is troublesome to ask each student to prepare his own material. If the sample of iron is in contact with moist air, it rusts quickly. Similarly with respect to the ferrous ammonium sulfate, $FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$, or ferrous sulfate, $FeSO_4 \cdot 7H_2O$, it is possible to purchase samples which are at least 99.9 per cent pure; but if the open bottle is allowed to stand in the air, some water of crystallization is usually lost and salts with so much water of crystallization are not ideal standards. For the purposes of instruction, "iron for standardization" or pure ferrous ammonium sulfate (Mohr's salt) can be used satisfactorily, but the student should bear in mind that, although the results of his analyses may agree perfectly, the actual values may be as much as 0.25 per cent of the total iron content in error when these faulty standards are used.

1. *Standardization against Pure Ferrous Ammonium Sulfate.* — Weigh out portions of 1.5–2.0 g of pure Mohr's salt, recording the weight to the nearest milligram. Add 10 ml of 6 N hydrochloric acid dilute and titrate promptly with potassium dichromate solution, using the same method of determining the end point as that chosen for the preliminary titration of dichromate against ferrous sulfate solution (p. 587). If the solution stands long it will become oxidized to some extent and become useless as a standard.

Since the equivalent weight of $FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$ is the molecular weight, 392.13, the normal concentration N of the dichromate solution will be found by the formula $\frac{p}{n \times 0.03921} = N$ when n milliliters of dichromate are used in titrating p grams of pure ferrous ammonium sulfate.

2. *Standardization against Iron.* — Weigh out accurately 0.24–0.26 g portions of pure, bright iron wire, handling it as little as possible, rolling it up so that it will not interfere with the free movement of the balance and discarding any rusty wire. Drop each weighed portion of wire into an Erlenmeyer flask containing 30 ml of 6 N hydrochloric acid. Place a small watch glass on the flask or, still better, a stemless, 40-mm funnel in the neck, and heat gently until all the wire is dissolved. Wash down the sides of the flask with a little hot water and add stannous chloride from a dropper until the solution is colorless,* but avoid adding an excess. Dilute with 150 ml of water, cool under the water faucet, and add 10 ml of mercuric chloride solution. Allow to stand about 2 minutes and titrate with dichromate, determining the end point as described on p. 587.

* There is usually a slight oxidation of the iron and formation of yellow ferric chloride, unless special pains are taken to exclude air during the heating and cooling.

$$4\,Fe^{++} + O_2 + 4\,H^+ \rightarrow 4\,Fe^{+++} + 2\,H_2O \qquad Fe^{+++} + 3\,Cl^- \rightleftarrows FeCl_3$$

The stannous chloride reduces the ferric salt:

$$2\,FeCl_3 + SnCl_2 = 2\,FeCl_2 + SnCl_4$$

and the excess reducing agent reacts with mercuric chloride to form a precipitate of mercurous chloride: $SnCl_2 + 2\,HgCl_2 \rightarrow \mathbf{Hg_2Cl_2} + SnCl_4$, provided a considerable excess of mercuric chloride is added. If, however, too much stannous chloride is present, some metallic mercury is precipitated;

$$SnCl_2 + HgCl_2 \rightarrow SnCl_4 + \mathbf{Hg}$$

and the analysis is spoiled; because the precipitated mercury dissolves in acid when an oxidizing substance is present. The mercurous chloride precipitate should be white and silky in appearance; if it is dark colored, discard the solution.

As reagents use a solution of 50 g $SnCl_2 \cdot 2H_2O$ in 100 ml of concentrated hydrochloric acid, and a solution of 27 g mercuric chloride in a liter of water.

From the net volume of potassium dichromate solution, n milliliters, required to oxidize a solution of ferrous salt from p grams of iron wire, compute the normality of the dichromate solution as follows:

$$\frac{p}{n \times 0.05584} = N$$

3. *Indirect Standardization against Sodium Oxalate.* — Either of the above methods of standardization will give results which are sufficiently accurate for practice with the potassium dichromate titrations. If, however, it is desired to get results which will be correct within less than 0.25 per cent of the total iron content (*e.g.*, if it is desired in the analysis of an iron ore containing 60 per cent Fe_2O_3 to get results which are within less than 0.15 per cent of the weight of sample), neither method is satisfactory. If the bottle containing the ferrous ammonium sulfate is left standing exposed to the air, and this will happen when a sample is kept in a phial under a cork stopper because cork, unless paraffined, is not impervious to air, there will be a gradual efflorescence of the crystals and as a result the iron content will become greater than the theoretical value of the pure salt. When iron wire is used as a standard, there may be some unobserved rust on the wire or there may be sufficient impurity in the metal to affect the results appreciably.

The Bureau of Standards will furnish at a reasonable price a sample of sodium oxalate which, when handled as directed, may be regarded as better than 99.99 per cent pure. The reaction between sodium oxalate and potassium dichromate cannot be used to serve as a *direct* method of standardization. In cold, dilute acid solutions, the oxalate ion is not oxidized quantitatively by dichromate. An indirect method, however, can be used.

Procedure. — Standardize a solution of potassium permanganate against pure sodium oxalate as directed on p. 547. With the aid of a pipet, transfer 25-ml portions of a ferrous sulfate solution (see p. 587) to each of four 400-ml beakers or 300-ml Erlenmeyer flasks. Titrate two of these portions against the potassium permanganate solution which has just been standardized and the other two portions against the potassium dichromate solution. Then if a milliliters of N_a-normal permanganate are used and b milliliters of the dichromate solution, the normal concentration N_b, of the latter is $\frac{a}{b} \cdot N_a = N_b$. Each of the above titrations should agree within 2 parts in 1000 of its duplicate, and the final results should be within 0.2 per cent of the truth.

Determination of Iron in Limonite

Weigh out accurately to four decimal places about 0.5 g of finely powdered ore into a small porcelain crucible. Using a small flame, roast the ore at dull redness for 5 minutes to destroy organic matter. Allow the crucible to cool, transfer the limonite to a small beaker, and remove the stain in the crucible by heating with four 5-ml portions of $6\,N$ hy-

drochloric acid. Heat the limonite with the acid until the residue no longer shows the limonite color. Add stannous chloride dropwise to the hot solution until the yellow color due to ferric chloride disappears and the solution is nearly colorless,* but avoid an excess. If more than 1 drop in excess is added, add a little potassium permanganate till a yellow color is obtained and repeat the reduction. Cool, dilute to 50 ml, and quickly add 8 ml of saturated mercuric chloride solution. Wait 3 minutes to make sure that the reaction is complete, transfer to a larger beaker, dilute to about 300 ml, and titrate with dichromate without further delay.

Determination of Chromium in Chromite

By fusion with sodium peroxide, the trivalent chromium is oxidized to chromate:

$$2\ FeCr_2O_4 + 7\ Na_2O_2 \rightarrow 2\ NaFeO_2 + 4\ Na_2CrO_4 + 2\ Na_2O$$

When the melt is leached with water, the iron is precipitated as ferric hydroxide and the chromate dissolves:

$$NaFeO_2 + 2\ H_2O \rightarrow NaOH + Fe(OH)_3$$

It is well to add a little more peroxide to make sure that the chromium is fully oxidized. Then the excess peroxide is decomposed by boiling the alkaline solution, the precipitate is dissolved in sulfuric acid, a known volume of standard ferrous sulfate is added, and the excess ferrous salt is titrated with dichromate.

Weigh out 0.3–0.5 g of ore into a 30–35 ml iron crucible and mix with about 4 g of sodium peroxide, using a dry stirring-rod. Remove any adhering powder from the rod by stirring about 1 g of sodium peroxide with it. Cover the mixture in the crucible with this last portion of peroxide. Place the lid on the crucible and gradually heat the contents to the melting point and maintain the fusion temperature for 5–6 minutes. Allow the melt to cool, place the crucible in a 300-ml beaker, and add 150 ml of cold water, keeping the beaker covered to avoid loss by effervescence.

When the fused mass has disintegrated, remove the crucible and wash it thoroughly. Add 0.5 g more of peroxide and gradually heat the liquid to boiling. Boil very gently for 15 minutes to make sure that all peroxide is decomposed. Allow the solution to cool somewhat, make distinctly acid to litmus and add 10 ml of 6 N sulfuric acid in excess. Dilute to 200 ml and add, from a clean pipet, which has been rinsed three times with a little of the solution, 25 ml of standard (approximately 0.1 N) ferrous ammonium sulfate solution. Stir and test a

* The addition of 3 ml of 0.5 per cent stannous chloride solution will hasten the dissolving of the limonite. It is important to avoid an excess of stannous chloride which will cause reduction of mercuric chloride to mercury and spoil the analysis.

drop of the solution on a white surface with fresh potassium ferricyanide solution. If no blue color is obtained, add another 25-ml portion of ferrous salt and continue adding it until an excess is present. Then titrate the excess with 0.1 N potassium dichromate solution.

On the same day that the analysis is made, take 25 ml of the ferrous solution, dilute to 300 ml, add 10 ml of 6 N sulfuric acid, and titrate with potassium dichromate solution. Compute the percentage of chromium present as follows:

Let a = milliliters of N-normal $K_2Cr_2O_7$ required to neutralize one pipetful of ferrous solution.
b = number of pipetfuls of ferrous solution used.
n = milliliters of $K_2Cr_2O_7$ used in the final titration.
s = weight of sample.
e = milli-equivalent wt. (0.01734 g Cr; 0.02534 g Cr_2O_3; 0.03731 g $FeCr_2O_4$).

$$(a \cdot b - n) N \times e \times 100 = \%$$

The analysis can be made with diphenylamine sulfonic acid as indicator. In this case it is necessary to add phosphoric acid, and proceed as described on p. 588 after adding enough ferrous salt to give a clear blue color to the solution.

The above-mentioned fusion with sodium peroxide is undoubtedly the most satisfactory method that has ever been proposed for the decomposition of refractory chromium minerals. The fusion can be made in an iron or nickel crucible; the iron one is soon spoiled, and even the nickel one does not last very long if the fusion is made over a free flame. A porcelain crucible has been recommended, and this has the advantage that then no iron oxide scale is formed which may possibly dissolve and react with the chromate. The attack of the nickel crucible can be prevented almost entirely by using as flux a mixture of sodium peroxide and sugar carbon, surrounding the crucible walls with cold water, and igniting the charge with a glowing string. Moreover, when the fusion is made in the following way it dissolves very rapidly in water.*

Muehlberg Method for Fusing Chromite with Sodium Peroxide

Mix 0.5 g of the ore in a 50-ml nickel crucible with 0.7 g of sugar carbon and 15 g of sodium peroxide. Use a dry spatula, hold it in an inclined position in the charge and, with the other hand, rotate the crucible. Care must be taken not to use more carbon or more chromite than indicated and to mix the charge well; it is not safe to attempt mixing in a mortar, as there is danger of an explosion. Tamp down

* W. F. Muehlberg, *Ind. Eng. Chem.*, **17**, 690 (1925). A similar method has been used for the determination of sulfur in coal and coke.

the charge using the flat, round stopper of a bottle. Place the crucible in a shallow pan and support it in a triangle, or place it in holes in the cover of the pan in such a way that the crucible is held firmly in place. Cover the crucible and fill the pan with water so that it comes nearly but not quite to the top of the crucible. Take off the cover with tongs held in the left hand; ignite the charge by touching it with the glowing end of a 10-cm-long string held in crucible tongs by the right hand. At once replace the cover of the crucible. The ignition should take place promptly. Keep the face away from the crucible and do not touch it with the fingers while it is hot. It is well to wear glasses, for when the charge is wrong the reaction is explosive.

As soon as the crucible is cool, remove it from the pan and, if the melt is not already detached, tap it sharply against a table. Transfer the melt to a 600-ml beaker. Fill the crucible, which now has very little material adhering to its walls, with water and pour the water into the beaker, quickly covering it. When the reaction of dissolving moderates, wash out the crucible with water and wash down the sides of the beaker. Dilute to 300 ml and boil to decompose all excess peroxide. Make the solution distinctly acid with sulfuric acid, and if there is any unattacked residue, filter it off, wash well with hot water, ignite, and weigh. Deduct this weight from the original weight of sample. Continue as described in the preceding directions, adding an excess of ferrous salt and titrating the excess with dichromate solution.

2. Determination of Manganese in Iron and Steel

*Method of J. Pattinson**

Principle. — If a solution containing iron, manganese, and calcium salts is treated with "chloride of lime" solution and calcium carbonate, all the iron and manganese are precipitated, the latter in the form of its hydrated dioxide. The entire precipitate can be dissolved in an acid ferrous sulfate solution of known strength, and the excess of the latter titrated with dichromate solution:

$$MnO_2 + 2\,Fe^{++} + 4\,H^+ \rightarrow Mn^{++} + 2\,Fe^{+++} + 2\,H_2O$$

$$1000 \text{ ml } N\,K_2Cr_2O_7 = \frac{Mn}{2} = 27.47 \text{ g Mn}$$

Procedure. — Dissolve 5 g of the iron or steel (or 1 g of ferromanganese) in hydrochloric acid, oxidize the solution with nitric acid, evaporate to a small volume, pour into a 100-ml measuring-flask, and dilute up to the mark with water. After thoroughly mixing, transfer 20 ml of the solution to a large beaker (of about 1-l capacity) and neutralize with pure calcium carbonate. Add the carbonate in small portions

* *J. Chem. Soc.*, **1879**, 365.

until the solution finally becomes a dark brown but still remains clear. After this add 50 ml of " chloride of lime " solution,* and more calcium carbonate with constant stirring until finally a little of the latter remains undissolved. To the slimy contents of the beaker, add 700 ml of hot water, and, after stirring, allow the insoluble residue to settle. If the supernatant liquid is violet, on account of the formation of calcium permanganate, add 1 or 2 drops of alcohol, boil, and again allow the precipitate to settle; in this case the upper liquid should be colorless. Decant the clear solution through a funnel containing a hardened filter paper and connected with suction. Wash the precipitate 4 times by decantation with 300 ml of hot water, then transfer to the filter without making any attempt to remove the last portions of the precipitate from the sides of the beaker, and wash with the aid of suction until the filtrate will no longer turn iodo-starch paper blue. Place the precipitate and filter in the original beaker, add 50 ml of a freshly standardized ferrous sulfate solution (cf. p. 587), and stir the liquid until the precipitate has entirely dissolved,† leaving behind the filter paper and sometimes small amounts of undissolved calcium sulfate. Titrate the excess of ferrous sulfate with potassium dichromate solution.

Assume that a grams of steel are dissolved in 100 ml of the solution and of this 20 ml were taken for the analysis. Assume that 50 ml of ferrous sulfate solution $= T$ milliliters 0.1 N $K_2Cr_2O_7$ and 50 ml ferrous sulfate + 0.2 a grams substance $= t$ milliliters 0.1 N $K_2Cr_2O_7$. Then

$$(T - t) \times 1.374 = \text{per cent Mn}$$

C. Iodometry

The fundamental reaction of iodometry is the following:

$$2\,Na_2S_2O_3 + I_2 = 2\,NaI + Na_2S_4O_6$$

or

$$2\,S_2O_3^{--} + I_2 \rightarrow 2\,I^- + S_4O_6^{--}$$

If to a solution containing a little iodine some starch solution is added, and sodium thiosulfate solution is run in from a buret, the blue color of the iodo-starch will disappear from the solution as soon as all the iodine has been reduced to iodide in accordance with the above equation. This is one of the most sensitive reactions used in analytical chemistry. If, therefore, a sodium thiosulfate solution of known strength is at hand,

* Prepared by shaking 15 g of fresh bleaching powder with 1 l of water and allowing the mixture to stand until the supernatant solution is clear.

† If the precipitate should not dissolve completely, add a little 18 N sulfuric acid until the brown color entirely disappears.

we have a means of determining not only iodine itself, but all of those substances (oxidizing agents) which when treated with potassium iodide set free iodine, or evolve chlorine when acted upon by hydrochloric acid. Consequently, iodometric processes are not only accurate but capable of most general application.

Under iodometry two kinds of methods are studied: (*a*) *direct methods*, in which iodine solution is used as the reagent and the end point is the blue color imparted to starch as soon as one drop of the reagent in excess has been added; and (*b*) *indirect methods*, in which an acid solution of some oxidizing agent is treated with an excess of potassium iodide, in which case iodine equivalent to the quantity of oxidizer present is liberated. In the direct methods, iodine is used as an oxidizing agent; in the indirect methods hydriodic acid is used as a reducing agent. Iodometric methods have, therefore, been applied to numerous reactions of oxidation and reduction. As a rule, these methods are sensitive and accurate. Direct iodometric methods are the oxidation of sulfurous acid to sulfuric acid, of hydrogen sulfide to free sulfur, of stannous chloride to stannic chloride, of arsenite to arsenate in a solution kept nearly neutral, and of trivalent antimony salt to the quinquevalent condition in a neutral solution. Indirect methods in which iodine equivalent to the substance analyzed is liberated by adding an excess of potassium iodide to the acid solution are illustrated by the determinations of bromine, chlorine, iodate, periodate, hypobromite, bromate, hypochlorite, chlorite, chlorate, persulfate, permanganate, hydrogen peroxide, nitrite, arsenate in strongly acid solutions, ferricyanide, chromate, permanganate, manganese dioxide, lead dioxide, minium or red lead, ferric ions, cupric ions, and antimonate ions.

The potential of the normal iodine/iodide system is -0.535 volt, which shows that iodine is a much weaker oxidizing agent than permanganate, ceric salt, or dichromate. Its potential does not depend upon the acidity of the solution, but the normal potentials of anions such as permanganate, dichromate, arsenate, antimonate, etc., do to a marked degree. For example, it is possible to oxidize arsenic quantitatively by iodine from the trivalent to the quinquevalent state if the p_H is kept between 4 and 9 but in the presence of considerable hydrochloric acid the reduction from the quinquevalent to trivalent state takes place completely upon adding an excess of potassium iodide.

The end point in iodometric processes is usually determined by the blue color of starch iodide which is formed when starch is present as soon as a very slight excess of iodine is present. In making titrations with iodine, therefore, starch can be added at the start and the approach of the end point will be shown by the formation of a dark blue color when the drop of iodine touches the solution but the color fades as the solution is stirred. At the end point, the color will not fade. In the indirect titrations, on the other hand, the starch should not be added until toward the end of the titration, when the presence of free iodine is not clearly shown by the lack of brown color.

Instead of starch, many chemists prefer to use carbon tetrachloride. One liter of pure water will dissolve only about 0.32 g of pure iodine, but the same quantity of CCl_4 will dissolve over 30 g of it. Iodine, therefore, is about 100 times as soluble in the CCl_4 as it is in water and the CCl_4 solution is very highly colored. When CCl_4 is added to a water solution it falls to the bottom of the vessel and does not dissolve appreciably. If the water contains a little dissolved iodine, then, on shaking the greater part of the iodine will dissolve in the CCl_4, because of its greater

solubility in it, and the color of the few drops of CCl_4 will be very much deeper than that of the original aqueous solution. Indirect iodometric titrations are, therefore, often made in a 250-ml glass-stoppered bottle. After adding the excess of potassium iodide, a little carbon tetrachloride is added and the titration with sodium thiosulfate is begun. At first the presence of iodine in the aqueous solution will be apparent, and gentle rotation of the liquid causes sufficient mixing. Toward the end of the titration, the bottle is stoppered and shaken after each addition of sodium thiosulfate and the end point is when the CCl_4 solution becomes colorless. In the distribution of a substance between two immiscible solvents, the ratio of the concentrations remains constant for a given molecular species. Therefore, as soon as some of the iodine is reduced in the aqueous layer by means of the thiosulfate, some of the iodine will pass from the CCl_4 to the water. Shaking the mixture helps to establish the equilibrium by breaking up the CCl_4 bubble and forcing it through all parts of the aqueous solution.

It was stated above that only about 0.32 g of iodine will dissolve in a liter of water. This corresponds to a normal concentration of 0.0025. By adding some potassium iodide to the solution, the solubility is increased greatly; thus by adding 65 g of KI to a liter of water as much as 35 g of iodine will dissolve, which corresponds to a normal concentration of 0.275, and if 100 g of KI are dissolved in 200 ml of water 153 g of iodine will dissolve. In the solution, the following reaction takes place to a considerable extent:

$$I_2 + I^- \rightarrow I_3^-$$

The reaction constant for this equilibrium has the high value of 770. The vapor pressure of the iodine from the aqueous solution is lowered by the formation of the tri-iodide anion and yet the solution as a reagent behaves exactly like free iodine. To a considerable extent the potassium iodide interferes with the dissolving out of the iodine by another solvent such as CCl_4 but not enough to prevent the determination of the end point as indicated above.

The Starch Solution

Triturate 0.5 g of *soluble starch* with a little cold water to a thin paste and rinse this into 25 ml of boiling water. Boil until a clear solution is obtained. A more stable-indicator solution can be prepared as follows:

Triturate 5 g of the solid into a paste with a little cold water, and slowly add to a liter of boiling water. Boil 1 or 2 minutes so that an almost clear solution is obtained. Cool by placing the dish in cold water, add 10 g of potassium iodide, and after allowing to stand over night filter the clear liquid into small 50-ml medicine bottles. Place these in a water-bath and fill up to the neck with the starch solution, heat 2 hours, and close by means of soft stoppers before removing from the hot-water bath. The solution thus sterilized can be kept almost indefinitely without the slightest trace of mold formation. Such a solution prepared according to the above directions by H. N. Stokes remained perfectly clear after standing 18 months and was as sensitive then as when first made up. After opening the bottle, mold begins to

form within one week, which explains why the solution is poured into small bottles; it may then be used before it becomes spoiled.

Sensitiveness of the Iodo-Starch Reaction

Iodine produces a blue color with starch only when hydriodic acid or a soluble iodide is present, and further, the formation of the blue color not only depends upon the presence of iodide but is largely influenced by the concentration of the iodide solution. With the same amount of iodide and different volumes of liquid quite different amounts of iodine are necessary to produce the blue color. From this it is evident that in any iodometric analysis about the same concentration should be maintained as in the standardization of the solutions used for the analysis. When $0.1\,N$ solutions are used, the error produced by not following this rule is a small one and for most purposes can be neglected. On the other hand, when an analysis is made with $0.01\,N$ solutions, a large error may be introduced and a blank should always be made to determine how much iodine solution is required to give an end point. The results of a series of experiments show that the amount of iodine solution necessary to produce the blue color in the absence of potassium iodide is directly proportioned to the dilution. If the solution contains 1 g of potassium iodide, a blue color will be produced by the same amount of iodine solution as long as not more than 150 ml of solution are present, but with a greater volume than that, more iodine is necessary independent of whether the solution contains 1 g or more of potassium iodide.

Preparation of Sodium Thiosulfate Solution

From the equation on p. 595 it is evident that an equivalent weight of iodine, the atomic weight in grams, is equal to 1 mole of $Na_2S_2O_3$. Hence, exactly 0.1 mole of crystallized sodium thiosulfate ($Na_2S_2O_3 + 5\,H_2O$) is required to make 1 l of tenth-normal solution.

A solution of pure sodium thiosulfate in " best " water will keep very well but thiosulfate solutions usually deposit sulfur on standing and the titer changes until the decomposition brought about by impurities is complete. The principal cause of the decomposition is bacterial action. Sterile solutions, free from carbon dioxide, keep indefinitely. The presence of about 3.8 g of borax per liter helps to keep the solution sterile.

Prepare the thiosulfate solution by dissolving the required amount of the commercial salt in freshly boiled water containing a little borax. If convenient, it is well to let the solution stand a week or so before determining its exact concentration.

The molecular weight of $Na_2S_2O_3 \cdot 5H_2O$ is 248.32. To prepare 1 l of 0.1 N solution 24.83 g of the salt are necessary, or, in round numbers, 25 g.

Standardization of Sodium Thiosulfate Solution

1. *With Copper Wire*

In technical work it is customary to standardize the thiosulfate solution against pure copper. Weigh out 0.2 g of pure Cu into a 200-ml Erlenmeyer flask and dissolve in 5 ml of 8 N HNO_3. Dilute with 25 ml of water and boil a few minutes to remove oxides of nitrogen. To remove the last of the nitrous oxides, add 5 ml of bromine water and boil until the excess bromine is expelled. Remove the flask from the flame and add strong ammonia until a slight excess is present. After boiling off the excess ammonia, add 7 ml of strong acetic acid, which dissolves any copper oxide that has deposited. Cool to room temperature, add 3 g of potassium iodide, and titrate the brown solution with sodium thiosulfate until nearly colorless, then add starch solution, and complete the titration. In making the titration for the first time, one is bothered somewhat by the fact that the cuprous iodide is usually colored a little by adsorbed iodo-starch and is not a pure white at the end point. If t milliliters of the thiosulfate solution were used in titrating a grams of copper, then 1 ml of thiosulfate $= \frac{a}{t}$ grams Cu and the thiosulfate solution is $\frac{}{t \times 0.06357}$ normal. The reactions that take place can be expressed as follows:

$$3\,\mathbf{Cu} + 8\,H^+ + 2\,NO_3^- \rightarrow 3\,Cu^{++} + 4\,H_2O + 2\,NO\uparrow$$
$$HNO_2 + Br_2 + H_2O \rightarrow HNO_3 + 2\,HBr$$
$$\rightarrow Cu(NH_3)_{\cdot}^{++}$$
$$^{+} + 4\,HC_2H_3O_2 \rightarrow Cu^{++} + 4 \qquad + 4\,C_2H_3O_2^-$$
$$2\,Cu^{++} + 4\,I^- \rightarrow \mathbf{Cu_2I_2} + I_2$$
$$I_2 + 2\,S_2O_3^{--} \rightarrow 2\,I^- + S_4O_6^{--}$$

Although 4 molecules of iodide react with 2 of copper, only 1 molecule of iodine is liberated. The equivalent weight of copper, therefore, corresponds to the reduction of *bivalent* copper to *univalent* copper and is the atomic weight of copper.

2. *With Pure Iodine*

Commercial iodine is contaminated with chlorine, bromine, water, and sometimes cyanogen; it must be purified. For this purpose grind

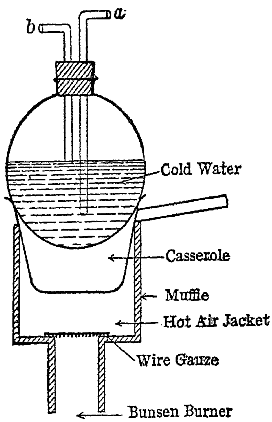

FIG. 114.

ting free an equivale
Place the mixture
(Fig. 114)* which rests in a muffle. Upon the casserole place a flask filled with cold water. Have a wire
of the muffle and a E
this.

As soon as the evolution of violet vapors from the bottom of the casserole has practically ceased, the sublimation is complete. Remove the flame and, after allowing to cool, take away the flask with the iodine adhering to it. To remove the iodine, pass a current of cold water through the tube *a* into the flask and out at *b*. This causes the glass to contract somewhat and the whole of the iodine crust can be removed by lightly scraping with a clean glass rod. Catch it upon a watch glass, break it up into large pieces, and repeat the sublimation without the addition of potassium iodide at as low a temperature as possible; in this way a product free from potassium iodide is obtained. Grind the iodine somewhat in an agate mortar and dry in a desiccator containing calcium chloride. If dried over sulfuric acid, some of the acid is likely to be present in the iodine. Furthermore, the cover of the desiccator must not be greased, for grease is attacked by iodine vapors, forming hydriodic acid, which might cause contamination.

The Weighing Out of the Iodine. — In each of 2 or 3 small weighing-tubes with tightly fitting glass stoppers place 2–2.5 g of pure potassium iodide free from iodate and 0.5 ml of water (not more); stopper the tubes and weigh accurately. Then open the tubes and add 0.4–0.5 g of pure iodine to each. Quickly insert the stopper and again weigh; the difference shows the amount of iodine. As the tubes are cooled by the dissolving of the iodine, moisture sometimes collects on the outside and must be wiped off before weighing. The iodine dissolves almost instantly in the concentrated potassium iodide solution. Place one of the tubes in the neck of a 500-ml Erlenmeyer flask which

* C. R. McCr... 0, 1664

is held in an inclined position and contains 200 ml of water and about 1 g of potassium iodide. Drop the tube to the bottom of the flask, but just as it begins to fall remove the stopper and allow it to follow. In this way no iodine is lost, which will be the case if the contents of a tube are washed into the water. A solution is thus prepared containing a known amount of iodine. To it add the sodium thiosulfate solution to be standardized from a buret until the liquid is pale yellow in color. Then add 2 or 3 ml of starch solution and carefully titrate until colorless. From the mean of 2 or 3 determinations, the strength of the thiosulfate solution is calculated.

If the weight of iodine equivalent to 1 ml of sodium thiosulfate solution is divided by 0.12693 (the milli-equivalent of iodine) the *normality* of the solution will be obtained.

3. *With Potassium Permanganate* (*Volhard*)

On adding potassium permanganate to an acid solution containing potassium iodide, the following reaction takes place:

$$2\,MnO_4^- + 10\,I^- + 16\,H^+ \rightarrow 2\,Mn^{++} + 8\,H_2O + 5\,I_2$$

The reaction is quantitative if the correct conditions are maintained.

Measure out 25–40 ml of standardized tenth-normal permanganate solution from a pipet or buret into a 300-ml Erlenmeyer flask containing 3 g of potassium iodide, 50 ml of water, and 5 ml of concentrated hydrochloric acid. Let stand in the dark for 3 minutes, dilute to 200 ml, and titrate slowly with the thiosulfate solution, adding 2 ml of starch indicator solution toward the last.

4. *With Potassium Dichromate*

The reaction between potassium dichromate and potassium iodide can also be used for the standardization of sodium thiosulfate solutions; the dichromate is reduced to green chromic salt, setting free an equivalent weight of iodine provided the solution is 0.2–0.4 N in acid.

$$Cr_2O_7^{--} + 6\,I^- + 14\,H^+ \rightarrow 2\,Cr^{+++} + 3\,I_2 + 7\,H_2O$$

Prepare tenth-normal potassium dichromate solution by dissolving 4.903 g of the pure, dry salt in water and diluting to 1 l at 20° in a measuring-flask. Mix well by pouring back and forth from the flask to a beaker at least 4 times. Measure out 20–40 ml of the dichromate solution, with a pipet or buret, into a 500-ml beaker containing 50 ml of water, 10 ml of concentrated hydrochloric acid, and 3 g of potassium iodide. Allow the reaction to proceed in the dark for 5 minutes,

then dilute to 400 ml and titrate with tenth-normal thiosulfate solution, adding starch toward the last.

5. *With Potassium Biiodate* (*C. Than*)*

If a solution of potassium biiodate is added to a solution of potassium iodide containing hydrochloric acid, the following reaction takes place:

$$\underbrace{KIO_3 \cdot HIO_3}_{389.95} + 10\,KI + 11\,HCl = 11\,KCl + 6\,H_2O + \underbrace{6\,I_2}_{1523}$$

If, therefore, 3.250 g of pure potassium biiodate are contained in 1 l of the aqueous solution, 10 ml of such a solution on being treated with an excess of potassium iodide and hydrochloric acid will set free exactly as much iodine as would be contained in 10 ml of 0.1 N iodine solution. By means of such a solution a known amount of iodine may be obtained at any time and in this way the solution of sodium thiosulfate may be standardized. At present it is possible to obtain commercially very pure potassium biiodate, but it is best to prepare a solution by weighing out 3.250 g per liter and determine the concentration accurately by titrating it against a solution of thiosulfate which has been freshly standardized against pure iodine. In this way a solution is obtained which can be conveniently used from time to time for testing the concentration of the thiosulfate solution.

Method of Titrating. — Place 1–2 g of pure potassium iodide in a beaker, dissolve in as little water as possible, and to this add 5 ml of 6 N hydrochloric acid, and then 20–25 ml of the biiodate solution (never in the reverse order). Iodine is liberated, immediately and quantitatively. Dilute with 200 ml of distilled water, and titrate the iodine as under 1.

Remark. — Instead of a solution of potassium biiodate, solid potassium iodate or potassium bromate can be used. One mole of each of these last two salts liberates 3 moles of I_2 when treated with potassium iodide and dilute acid.

Preparation of Tenth-normal Iodine Solution

No advantage is obtained by dissolving the desired quantity of sublimed iodine in a definite volume of solution, for the latter cannot be kept very long unchanged. It is more practical to prepare the iodine solution by placing 20–25 g of pure potassium iodide in a liter bottle dissolving it in as little water as possible and then adding about 12.7 g of commercial iodine, weighed out roughly on a watch glass. Shake the contents of the flask until all the iodine is dissolved. When this is

* *Z. anal. Chem.*, **16**, 477 (1877).

accomplished, dilute the solution to about 1 l and standardize according to one of the following methods.

Standardization of Iodine Solution

1. *With 0.1 N Sodium Thiosulfate Solution*

Take 25 ml of the well-mixed iodine solution in a 250-ml Erlenmeyer flask, dilute to 100 ml and introduce 0.1 N $Na_2S_2O_3$ solution until nearly all the iodine has reacted as shown by the color. Add 2 ml of starch paste and titrate slowly until colorless.

Remark. — To titrate a solution of iodine obtained from a solution of iodide-iodate mixture, titrate in the same way but in the presence of 20 millimoles of free hydrochloric acid.

2. *With Arsenious Acid*

If iodine is allowed to act upon a neutral solution of arsenious acid the reaction which takes place may be expressed as follows:

$$+ I_2 + 2\,HCO_3^- = H_2AsO_4^- + 2\,I^- + H_2O + 2\,CO_2$$

It is necessary to keep the solution neutral or the opposite reaction will take place.

$$H_2AsO_4^- + 2\,I^- + 6\,H^+ = As^{+++} + I_2 + 4\,H_2O$$

In a neutral solution arsenite can be oxidized quantitatively by means of free iodine but in strongly acid solution arsenic acid can be reduced quantitatively to the trivalent condition by means of iodide. To accomplish a complete oxidation of the arsenic by iodine, it is necessary to keep the solution approximately neutral to phenolphthalein. This is usually accomplished by providing an excess of sodium bicarbonate, by adding normal sodium carbonate to the cold, acid solution, or by adding some disodium phosphate. Caustic alkali cannot be used because it reacts with iodine to form hypo-iodite and iodide. A little neutral sodium carbonate does no harm if added to an acid solution because the liberated carbon dioxide neutralizes the hydroxyl ion formed by hydrolysis of the carbonate.

From the above equation, and the fact that the valence change of arsenic is 2, it follows that the equivalent weight of arsenic is one-half the atomic weight. Ordinarily, the arsenite solution is prepared by weighing out pure As_2O_3. As the molecule contains 2 atoms of arsenic, it is evident that one-fourth the molecular weight in grams is the equivalent weight of As_2O_3.

To prepare 0.1 N arsenious acid solution, dissolve 4.95 g of the pure sublimed oxide and 15 g of sodium carbonate by warming with 150

ml of water. Transfer the solution to a liter measuring-flask, add 25 ml of normal acid, and dilute at 20° to the mark.

To prepare pure arsenious oxide from the commercial product, sublime by heating in a porcelain dish and collect the sublimate on a watch glass. If a yellow sublimate of sulfide is noticed, dissolve the sample in hot $4N$ hydrochloric acid, filter off the undissolved sulfide, and cool the filtrate to cause crystals to deposit. Filter, wash with water, and then sublime. Dry over calcium chloride in a desiccator.

Titrate the arsenite against the iodine solution in the usual way. Deiss,* however, finds that iodine gradually changes to iodate on standing and the iodate does not react with arsenic in the presence of sodium bicarbonate. He proceeds as follows:

Add 25 ml of the iodine solution to 200 ml of water. Add 2 ml of $6N$ hydrochloric acid and then 2 g of sodium bicarbonate. As soon as it has dissolved titrate with sodium arsenite.

A solution of sodium arsenite gradually oxidizes on long standing.†

3. *With Anhydrous Sodium Thiosulfate*‡

Anhydrous sodium thiosulfate may be prepared in a state of sufficient purity to permit its use for standardizing iodine solutions. Prepare a saturated filtered solution of the commercial salt at 30° to 35° and then cool while stirring constantly. Collect the salt that deposits; dry over sulfuric acid until it falls to a powder and a little of it in a test-tube shows no sign of fusion when heated to 50°. Effect the final dehydration by heating at 80° with repeated stirring of the powder.

Young standardized a solution of iodine by this method and obtained the same value as by titrating against a thiosulfate solution which had been standardized against pure iodine.

Analyses by Iodometric Methods

1. Determination of Free Iodine

1000 ml of 0.1 N thiosulfate solution = 12.69 g I

Dissolve the iodine in a solution of potassium iodide and titrate either with sodium thiosulfate or with arsenious acid exactly as described under the standardization of an iodine solution.

* *Chem. Ztg.* **38**, 413.

† *Ibid.*, **36**, 713 (1912).

‡ S. W. Young, *J. Am. Chem. Soc.*, **26**, 1028 (1904).

2. Determination of Chlorine in Chlorine Water

1000 ml of 0.1 N thiosulfate solution = 3.546 g Cl

Add a measured amount of chlorine water to a solution containing an excess of potassium iodide. Hold the point of the pipet just above the surface of the iodide solution contained in a glass-stoppered bottle. After the chlorine water has been added, stopper the bottle, vigorously shake the contents, and titrate the liberated iodine with sodium thiosulfate as above:

$$2\,KI + Cl_2 = 2\,KCl + I_2$$

3. Determination of Bromine in Bromine Water

1000 ml of 0.1 N thiosulfate solution = 7.992 g Br

The procedure is the same as under 2:

$$2\,KI + Br_2 = 2\,KBr + I_2$$

4. Determination of Hypochlorous Acid in the Presence of Chlorine

The determination is based upon the following reactions:

$$HOCl + 2\,KI = KCl + KOH + I_2$$
$$Cl_2 + 2\,KI = 2\,KCl + I_2$$

One mole of hypochlorous acid liberates 1 mole of iodine, but produces at the same time 1 mole of potassium hydroxide, while the chlorine simply sets free an equivalent amount of iodine. After neutralizing the alkali by means of an excess of hydrochloric acid and determining the iodine by titration with sodium thiosulfate, the excess of hydrochloric acid is titrated with standard alkali solution.

Procedure. — Add a measured excess of 0.1 N hydrochloric acid to a potassium iodide solution, and to this add a known amount of the mixture of chlorine and hypochlorous acid. Titrate the iodine set free with 0.1 N thiosulfate solution. Then add methyl orange to the colorless solution and titrate the excess of hydrochloric acid with 0.1 N NaOH. The alkali hydroxide produced by the action of the hypochlorous acid upon the iodide requires half as much 0.1 N acid for neutralization as is required of 0.1 N $Na_2S_2O_3$ solution to react with the iodine set free by the action of the hypochlorous acid.

Example. — If V milliliters of chlorine + hypochlorous acid were taken for analysis, t milliliters 0.1 N HCl were added at the start, T milliliters 0.1 N $Na_2S_2O_3$ used for titrating the iodine, and t_1 milliliters 0.1 N NaOH for titrating the excess of acid, then $t - t_1$ milliliters of 0.1 N acid were required to neutralize the alkali hydroxide and $2\,(t - t_1)$ milliliters of 0.1 N $Na_2S_2O_3$ to react with the iodine formed from the hypochlorite.

Hence $(t - t_1)\ 0.005247^* = \text{g HOCl in } V$ milliliters solution

and

$$T - 2\ (t - t_1)\ 0.003546 = \text{grams Cl in } V \text{ milliliters solution}$$

5. Determination of Iodine in Soluble Iodides†

(a) *By Decomposition with Ferric Salts*

If a solution of a soluble iodide is treated with an excess of ferric-ammonium alum and acidified with sulfuric acid, the ferric salt will be reduced to ferrous salt with separation of iodine:

$$Fe_2(SO_4)_3 + 2\,HI = H_2SO_4 + 2\,FeSO_4 + I_2$$

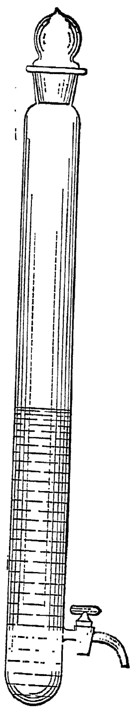

Fig. 115.

If the solution is heated to boiling, the iodine escapes with the steam and can be collected in a solution of potassium iodide and then titrated with sodium thiosulfate or arsenious acid. This method is suited for separating iodine from bromine, for bromides do not reduce ferric salts. The bromide will be found in the residue obtained after the distillation, and is best determined gravimetrically.

(b) *By Decomposition with Nitrous Acid (Fresenius)*

This excellent method, which is especially suited for determining small amounts of iodine in the presence of bromine and chlorine in mineral waters, depends upon the easy oxidation of hydriodic acid by means of nitrous acid:

$$2\,HI + 2\,HNO_2 = 2\,H_2O + 2\,NO + I_2$$

Hydrochloric and hydrobromic acids are not attacked by nitrous acid.

Procedure. — To the small apparatus shown in Fig. 115 transfer the neutral or slightly alkaline solution of the iodide; make slightly acid with dilute sulfuric acid, and add a little freshly distilled, colorless carbon bisulfide (carbon tetrachloride or chloroform), so that it does not quite reach to the stopcock, near the bottom of the tube. Then introduce 2, or at the most 3, drops of "nitrose,"‡ stopper the tube, shake

---

* $HOCl = 52.47$; 1 ml 0.1 N solution $\doteq$ 0.005247 g HOCl (against NaOH).

† In the case of insoluble iodides, the metal must first be removed if the iodine is to be determined volumetrically. This can be accomplished by the method of Mensel (*Z. anal. Chem.*, **12**, 137). It may be said, however, that the volumetric method offers no advantages over the gravimetric one.

‡ Cf. Vol. I.

vigorously, and then allow the carbon bisulfide to settle once more. The small amount which at first adheres to the glass sides can be made to fall to the bottom by revolving and inclining the tube. On the upper surface of the liquid there will still remain a few tiny drops of carbon bisulfide. To obtain these, moisten a filter with water and place the funnel under the glass stopcock, remove the stopper from the tube, and allow the aqueous solution to run through the filter; the carbon bisulfide will remain behind on the paper. Shake the carbon bisulfide remaining in the tube 3 times with successive portions of distilled water, and each time allow the water to run off through the same filter. Then place the funnel at the top of the tube, puncture the filter with a pointed glass rod, and wash the carbon bisulfide into the tube by means of about 0.5 ml of water. After this add 1 or 2 drops of sodium bicarbonate solution and thoroughly shake with the carbon bisulfide, then add standard sodium thiosulfate solution until the reddish violet carbon bisulfide solution becomes colorless.

The value of the sodium thiosulfate solution is not determined as ordinarily, but by means of a potassium iodide solution treated as above described.

Remark. — This method is useful for determining small amounts of iodide in the presence of relatively large amounts of chloride and bromide, as in the analysis of mineral waters. For the standardization of the sodium thiosulfate solution, as nearly as possible the same amount of potassium iodide should be used as is present in the unknown solution; this is determined by the color of the carbon bisulfide. Pure potassium iodide must be used for this purpose, and its purity tested by means of a gravimetric determination of the iodine present in the salt after it has been dried at 170°–180°.

The reason the sodium thiosulfate solution must be standardized in this way is as follows:

When an aqueous solution containing iodine is shaken with carbon bisulfide, not all of the iodine but the greater part of it will pass into the solvent. The error is compensated, however, by standardizing the solution in the same way.

If the solution of a substance is shaken with another solvent in which the former does not mix, the original amount of the substance divides itself between the two solvents, and in fact the concentration of one solution (amount of the dissolved substance present per milliliter) always bears a constant relation to that of the other.

Thus if x_0 grams of iodine are dissolved in V milliliters of water, and the solution is shaken with V_1 milliliters of carbon bisulfide, then x_1 grams of iodine will remain in the aqueous solution and $x_0 - x_1$ grams will pass into the carbon bisulfide.

The amount x_1 is found by the following equation:

$$(1)\quad \frac{x_1}{V} = \frac{x_0 - x_1}{V_1}k \qquad \text{and} \qquad x_1 = x_0\frac{kV}{V_1 + Vk}$$

$\frac{x_1}{V}$ and $\frac{x_0 - x_1}{V_1}$ are the concentrations in each of the solutions, and k is the *distribution*

coefficient, which is $\frac{1}{400}$ for iodine.* If the aqueous solution is now shaken with the same amount of fresh carbon bisulfide, then x_2 grams of iodine will remain in the water and $x_1 - x_2$ will be extracted by the carbon bisulfide. In this case, however,

$$(2) \quad x_2 = x_0\left(\frac{kV}{V_1 + Vk}\right)^2 \text{ grams iodine}$$

so that after shaking n times with fresh portions of carbon bisulfide, the amount of iodine remaining in the water would be:

$$(3) \quad x_n = x_0\left(\frac{kV}{V_1 + Vx}\right)^n \text{ grams iodine}$$

Assuming that in the analysis 0.005 g of iodine was dissolved in 10 ml of water and that this solution was shaken once with 1 ml of carbon bisulfide, then according to equation (1)

$$x_1 = 0.005\,\frac{\frac{1}{400} \times 10}{1 + \frac{10}{400}} = 0.005 \cdot \frac{1}{41} = 0.0001 \text{ g iodine}$$

would remain dissolved in the water, or an amount that can be neglected. The distribution coefficient, as used above, holds when the same molecular species is present in each solvent. When potassium iodide is added to the aqueous solution, KI_3 is formed and it is much harder to dissolve out the iodine. As some potassium iodide is present, the above calculation is inexact.

If, after shaking with carbon bisulfide, the aqueous solution still appears yellow, it must be treated a second, and perhaps a third, time with fresh amounts of carbon bisulfide.

6. Determination of Bromine in Soluble Bromides (Bunsen)

If chlorine water is added to a colorless bromide solution in a porcelain dish, the solution becomes yellow:

$$2\,KBr + Cl_2 = 2\,KCl + Br_2$$

If it is heated to boiling, the bromine is expelled and the solution becomes colorless again. The addition of the chlorine water is continued until finally no yellow coloration is produced.

Preparation and Standardization of the Chlorine Water

Dilute 100 ml of a saturated chlorine water to 500 ml and titrate against a weighed amount of pure potassium bromide which has been dried at 170°, taking about the same amount of bromide for the standardization as is supposed to be present in the solution to be analyzed. During the titration, wrap the buret containing the chlorine water in black paper to protect its contents from the light, and hold the tip of the buret just above the surface of the hot bromide solution, so that as little chlorine as possible is lost by evaporation.

* Berthelot and Jungfleisch, *Compt. rend.*, **69**, 338.

7. Determination of Iodine and Bromine in Mineral Waters

According to the amount of halogen present, take 5–60 l of water for the analysis. The amount of bromide and iodide present is usually small compared with the chloride, so that the residue obtained by the evaporation of a large amount of water cannot be used directly for the analysis, but by partial crystallization a mother-liquor rich in bromide and iodide must first be obtained.

Procedure. — Pour the water into a large evaporating-dish, a liter at a time, and if not already alkaline,* add enough pure sodium carbonate solution to make it distinctly so, and evaporate to about one-fourth of its original volume. This causes the separation of some calcium and magnesium carbonates, as well as hydroxides of iron and manganese, but all the halogen salts remain in solution. Filter off the residue and thoroughly wash with water. Concentrate the filtrate further until salts begin to crystallize out, and pour the hot solution into 3 times its volume of absolute alcohol; this causes the greater part of the sodium chloride and other undesired salts to precipitate. After standing 12 hours, filter the alcoholic liquid and wash the residue 5 or 6 times with 95 per cent alcohol.

To the alcoholic solution, which contains all the iodine and bromine with considerable chlorine in the form of the alkali salts, add 5 drops of concentrated potassium hydroxide solution and distil off most of the alcohol, while passing a current of air through the solution by means of a capillary tube reaching to the bottom of the liquid in the distilling-flask.

Evaporate the residue from the distillation until salts again begin to crystallize out and repeat the precipitation with alcohol. Again distil off the alcohol, but this time with the addition of only 1 or 2 drops of potassium hydroxide solution. According to the amount of salts present in solution repeat this operation 3–6 times. Place the final filtrate, after the alcohol has been distilled off, in a platinum dish, evaporate to dryness, cover the dish with a watch glass, and gently ignite the residue to destroy organic matter. Dissolve the residue from the ignition in a little water, filter off the carbonaceous material,† make the solution slightly acid with dilute sulfuric acid, titrate the iodine liberated by the addition of 1 or 2 drops of "nitrose," and with sodium thiosulfate, after shaking with chloroform, as described on p. 606.‡ Determine bromine in the aqueous solution obtained after the

* The solution is alkaline if after the addition of phenolphthalein the solution turns red on boiling.

† If the filtrate is not completely colorless, evaporate and again ignite.

‡ Lecco determines the iodine colorimetrically (*Z. anal. Chem.*, **35**, 318).

extraction of the iodine with chloroform. Make the acid solution alkaline by the addition of sodium carbonate solution, add 2 drops of a saturated sugar solution, and evaporate the solution to dryness in a platinum dish. With a watch glass upon the dish, gently ignite the residue to destroy the sugar and the excess of nitrite.* After this has been accomplished dissolve the residue in water, filter, make slightly acid with sulfuric acid, and titrate the bromide with chlorine water as described on p. 608.

Remark. — If sufficient mineral water is available it is better to divide the mother-liquor containing the bromide and iodide into two portions; in one portion determine the iodine as above, and in the other determine bromine and iodine by titration with chlorine water.†

8. Analysis of Peroxides (Bunsen)

All peroxides of the heavy metals which evolve chlorine on treatment with hydrochloric acid can be determined with great accuracy by conducting the chlorine into potassium iodide solution and titrating the liberated iodine with sodium thiosulfate or arsenious acid solution. It is only necessary to make sure that the chlorine is allowed to act upon the potassium iodide without loss. For all such determinations, Bunsen employed the apparatus shown in Fig. 116. The small decomposition flask of about 40-ml capacity has a ground-glass connection with the delivery tube‡ and is held firmly in place by means of rubber rings, as at *a*. The lower end of the bent delivery tube is drawn out into a not-too-small capillary.

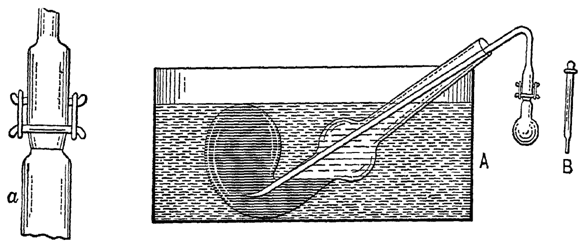

FIG. 116.

Procedure. — Place the finely powdered substance in the small glass-stoppered weighing-tube (Fig. 116 *B*), which has a small piece of glass

* The addition of the sugar causes the nitrite to be destroyed at a lower temperature than would otherwise be the case, and the danger of losing bromine by volatilization is avoided.

† As the chlorine water was standardized against bromide, an amount of the latter equivalent to the iodine present should be deducted from the amount represented by the chlorine water used; the difference shows the bromine present.

‡ Instead of the ground-glass connection, Bunsen used a tube of the same size as the neck of the flask and connected them with rubber tubing, the two glass tubes being against one another.

fused on the end, and weigh. Take hold of the tube by the glass at the bottom,* introduce it into the neck of an absolutely dry decomposition flask, and allow the required amount of the substance to fall into it by carefully revolving the weighing-tube. Again weigh the tube, to determine the amount of substance taken. Add hydrochloric acid (its concentration depends upon the nature of the substance), at once connect the delivery tubing with the flask, and introduce it into the retort containing potassium iodide solution. By means of a tiny flame, heat the contents of the flask to boiling and distil half to two-thirds of the liquid over into the retort. To prevent the iodide solution from sucking back into the flask, take out the delivery tube from the retort before removing the flame, and wash the contents of the tube into the retort.

Pour the potassium iodide solution into a large beaker, rinse out the retort several times with a little water, and then with potassium iodide solution to remove any iodine which may remain adhering to the glass. Titrate with 0.1 *N* sodium thiosulfate solution using starch as indicator. In this way pyrolusite, chromates, lead peroxide, minium, ceric oxide, selenic, telluric, and molybdic acids may be analyzed.

(*a*) Determination of Manganese Dioxide in Pyrolusite

1000 ml of 0.1 *N* $Na_2S_2O_3$ solution $\frac{{}_2}{20} = 4.347$ g MnO_2

Weigh out about 0.2 g of the substance which has been dried at 120°. To this add 25 ml of 4 *N* hydrochloric acid and carry out the analysis as described above.

$$\mathbf{MnO_2} + 4\,HCl = 2\,H_2O + MnCl_2 + Cl_2$$
$$Cl_2 + 2\,KI = 2\,KCl + I_2$$

If t milliliters of 0.1 *N* $Na_2S_2O_3$ were used in titrating a grams of MnO_2, then

$$\frac{0.4347\,t}{a} = \text{per cent } MnO_2$$

The determination of chromates, lead peroxide, and selenic acid is carried out in the same way, except that 12 *N* hydrochloric acid is used for the decomposition.

Instead of the apparatus shown on p. 610, Rupp† uses a 50-ml distilling-flask for the decomposition and 750-ml bottle as receiver; the bottle contains 250 ml of

* By holding the tube in this way, deviations of weight, due to unequal warming, are avoided.

† *Chem.-Ztg.*, **52**, 429 (1928).

1 per cent potassium iodide solution. The arm of the distilling-flask is fused to 18–20 cm of tubing with about 3-mm inside diameter, and this long arm is bent downward so that the interior angle is about 135° and the tube will easily reach the bottom of the receiving bottle. The long arm is inserted in one hole of a twice-bored rubber stopper that fits the receiver. The other hole of the stopper is fitted with a tube containing glass beads and some glass wool. The top of the distilling-flask carries a stopper enclosing a tube which reaches to the bottom of the flask with a 1-mm opening at the bottom. The top of this tube is closed with a pinchcock on rubber tubing, 0.2 g of the pyrolusite is introduced into the distilling-flask, taking care not to get any powder on the sides. Twenty-five milliliters of strong hydrochloric acid are introduced and the stopper inserted quickly. The acid is heated with a small flame, protected from drafts, until the volume is reduced one-half. Then the pinchcock is opened to prevent the liquid sucking back, the flame is removed, and the contents of the receiver are titrated with thiosulfate. It is well to put a few crystals of potassium iodide on top of the glass wool in the drying-tube. Then, if this is moistened, it will show if any iodine is lost by volatilization.

(*b*) Determination of Telluric Acid

If the telluric acid is present as the hydrous acid ($H_2TeO_4 + 2\,H_2O$) or as tellurate, the analysis is performed in the same way as with selenic and chromic acids. If, however, the tellurium is present as the anhydrous acid or as the anhydride, the method must be modified, for these substances are scarcely attacked by concentrated hydrochloric acid. They are placed in the decomposition flask and dissolved in a little concentrated potassium hydroxide;* to the tellurate solution thus obtained the concentrated hydrochloric acid is added, and the reduction then is accomplished without difficulty:

$$K_2TeO_4 + 4\,HCl = 2\,KCl + H_2TeO_3 + H_2O + Cl_2$$

According to this equation, 1 l of $0.1\,N$ $Na_2S_2O_3$ = 6.375 g Te = 7.975 g TeO_2.

(*c*) Determination of Ceric Oxide

$$1000 \text{ ml of } 0.1\,N \text{ iodine solution} = \frac{CeO_2}{10} = 17.21 \text{ g } CeO_2$$

Ceric oxide when mixed with considerable lanthanum and didymium oxides is reduced by distillation with concentrated hydrochloric acid: $2\,CeO_2 + 8\,HCl = 4\,H_2O + 2\,CeCl_3 + Cl_2$.

If, however, the mixture contains but little of the two last substances, or if it is pure ceric oxide, the heating with concentrated hydrochloric acid is of no avail; the ceric oxide will not dissolve.

In the presence of hydriodic acid, however, the reduction takes place readily, so that it is only necessary to add 2 g of potassium iodide

* The solution could not be effected by using *sodium* hydroxide.

to a weighed amount of the substance (0.67–0.68 g) in the decomposition flask, and then, after the addition of hydrochloric acid, violet vapors of iodine can be distilled from the solution:

$$2\,CeO_2 + 2\,KI + 8\,HCl = 2\,KCl + 2\,CeCl_3 + 4\,H_2O + I_2$$

Often so much iodine will be given off that the solid is likely to stop up the tube and the flask may explode. To prevent this, do not draw out the end of the delivery tube into a capillary, but at the bottom leave an opening of about 4 mm in diameter. During the operation, the flame must be protected from air-currents, for otherwise there is danger of liquid sucking back from the retort.

(*d*) Determination of Vanadic Acid*

$$1000 \text{ ml of } 0.1\,N \text{ iodine solution} = \frac{\quad}{20} = 9.096 \text{ g } V_2O_5$$

By boiling vanadic acid, or one of its salts, with concentrated hydrochloric acid, the vanadium is reduced with evolution of chlorine. Unfortunately, this reaction cannot be used for the determination of vanadic acid, for the amount of chlorine evolved depends upon the concentration of the vanadium solution; the vanadium is not reduced to a definite oxide. On the other hand, by means of *hydrobromic* acid,† vanadic acid is reduced to a blue vanadyl salt:

$$2\,H_3VO_4 + 2\,HBr + 4\,HCl = V_2O_2Cl_4 + 6\,H_2O + Br_2$$

If the free bromine is absorbed in potassium iodide, and the liberated iodine titrated with sodium thiosulfate, a sharp determination of the vanadium will be obtained. To carry out this analysis, place 0.3–0.5 g of the vanadate, together with 1.5–2 g of potassium bromide, in the decomposition flask of the Bunsen apparatus (Fig. 116, p. 610), add 30 ml of concentrated hydrochloric acid, and distil as before. The decomposition is always complete when the liquid in the flask is a pure blue.

If hydriodic acid is used instead of hydrobromic acid, the vanadic acid is reduced still further, almost to VCl_3.‡ In fact, a complete reduction can be accomplished if potassium iodide, concentrated hydrochloric acid, and 1 or 2 ml of sirupy phosphoric acid are added and the liquid distilled until no more vapors of iodine are evolved. According to Steffan, this will always be the case when the liquid is reduced to one-third of its original volume.

* Friedheim and Euler, *Ber.*, **28**, 2067 (1895), and **29**, 2981 (1896).

† Holverscheidt, *Dissertation*, Berlin, 1890.

‡ Friedheim and Euler, *Ber.*, **28**, 2067 (1895).

(e) Determination of Molybdic Acid

$$1000 \text{ ml of } 0.1\, N\; Na_2S_2O_3 = \frac{MoO_3}{10} = 14.4 \text{ g } MoO_3$$

The determination depends upon the fact that molybdic acid is reduced to the quinquevalent state by means of hydriodic acid with liberation of iodine:

$$2\, MoO_3 + 2\, HI + 10\, HCl = 2\, MoCl_5 + 6\, H_2O + I_2$$

Remark. — This method finds no practical application on account of the fact that it is difficult to obtain a quantitative reduction in accordance with the above equation. Gooch and Fairbanks* found that if a solution containing molybdic acid is distilled in the Bunsen apparatus with potassium iodide and hydrochloric acid until iodine vapors are no longer visible and the solution is a light green, too little iodine is obtained. On the other hand, they found that, if the distillation is continued still further, the reduction goes on and more iodine is obtained than corresponds to the above equation. Steffan,† who tested the method in the author's laboratory, obtained results agreeing with those published by Gooch and Fairbanks. By means of *hydrobromic* acid, molybdic acid is not reduced.

(f) Determination of Vanadic and Molybdic Acids in the Presence of One Another

According to Steffan, these two acids may be determined very accurately when present together. The vanadic acid is determined, according to Holverscheidt, by distillation with potassium bromide and concentrated hydrochloric acid, absorption of the bromine in potassium iodide solution, and titration of the liberated iodine (cf. p. 613). The contents of the distillation flask, in which the vanadium is present as vanadyl salt and the molybdenum as molybdic acid, are treated with hydrogen sulfide in a pressure flask, and the precipitated molybdenum sulfide is filtered through a Gooch crucible, and weighed as MoO_3, as described on p. 274. The results obtained by this method are perfectly satisfactory.

As molybdic acid is unattacked by hydrobromic acid, but is reduced to the quinquevalent state with separation of iodine by means of hydriodic acid, Friedheim and Euler proposed to carry out the analysis by first reducing the vanadium to vanadyl salt by treatment with potassium bromide and hydrochloric acid and determining the liberated bromine iodometrically. Then it was attempted to reduce the vanadium to VCl_3 and the molybdenum to $MoCl_5$ by adding KI, HCl, and H_3PO_4 and distilling until no more iodine is given off and the solution is a light green.

* *Z. anorg. Chem.*, **13**, 101 (1897), and **14**, 317.

† Steffan, *Inaug. Dissertation*, Zürich, 1902.

The error in the method lies in the fact that the vanadic acid is reduced completely to V_2O_3 only when the solution is distilled to one-third of its original volume and the molybdenum is then reduced further than corresponds to the formation of $MoCl_5$.

9. Analysis of Chlorates

$$1 \text{ l of } 0.1\,N\ Na_2S_2O_3 = \frac{KClO_3}{60} \quad 2.043 \text{ g } KClO_3$$

This is carried out the same way as the analysis of pyrolusite (cf. p. 611): $KClO_3 + 6\,HCl = KCl + 3\,H_2O + 3\,Cl_2$.

Many oxidizing agents can be determined iodometrically without previous distillation with hydrochloric acid.

For other methods of analyzing chlorates iodometrically, consult H. Dietz, *Chem.-Ztg.*, **1901**, 727, and Luther and Rutter, *Z. anal. Chem.*, **46**, 521 (1907).

10. Determination of Hypochlorous Acid

This determination is used in the analysis of chloride of lime.

Procedure. — Into a tared weighing-tube introduce about 5 g of "chloride of lime," and weigh the stoppered tube. Wash into a porcelain dish, rub to a paste with a pestle, and transfer without loss to a 500-ml measuring-flask. Dilute to the mark with water, and shake well. Of this turbid solution, pipet off 20 ml into 10 ml of 10 per cent potassium iodide solution, make acid with hydrochloric acid, titrate the liberated iodine with 0.1 N $Na_2S_2O_3$. Express the result in percentage of *available chlorine.*

Remark. — If the "chloride of lime" contained calcium chlorate it will be partially reduced by hydrochloric acid and potassium iodide with liberation of iodine, and consequently the results obtained for hypochlorite chlorine (bleaching chlorine) will be too high. In this case the hypochlorite is best determined by a chlorimetric process with arsenious acid (see p. 649).

11. The Analysis of Iodates

$$1 \text{ l of } 0.1\,N\ Na_2S_2O_3 = \frac{HIO_3}{60} = 2.932 \text{ g } HIO_3$$

Allow the solution of the iodate to run into an acid solution containing an excess of potassium iodide. Iodine is set free according to the equation: $KIO_3 + 5\,KI + 6\,HCl = 6\,KCl + 3\,H_2O + 3\,I_2$. Titrate the iodine with thiosulfate solution as described on p. 601.

12. The Analysis of Periodates

$$1 \text{ l of } 0.1\ N\ Na_2S_2O_3 = \frac{HIO_4}{80} = 2.399 \text{ g } HIO_4$$

The analysis of periodates is carried out exactly as with iodates; the reaction that takes place is

$$KIO_4 + 7\ KI + 8\ HCl = 8\ KCl + 4\ H_2O + 4\ I_2$$

13. Analysis of a Mixture of Iodate and Periodate*

If a neutral or slightly alkaline solution of an alkali periodate is treated with a solution of potassium iodide, the following reaction takes place:

$$KIO_4 + 2\ KI + H_2O = 2\ KOH + KIO_3 + I_2$$

The liberated iodine is titrated with tenth-normal arsenious acid (not with sodium thiosulfate); in a neutral solution the *iodate* does not react with potassium iodide. For the analysis of a mixture of iodate and periodate, the following procedure is used:

In one sample determine the iodate + periodate by adding the solution of the substance to an acid solution containing an excess of potassium iodide and titrate the liberated iodine with sodium thiosulfate solution.

Dissolve a second sample in water, add a drop of phenolphthalein indicator, and make the solution alkaline enough to give the pink color with phenolphthalein, adding alkali if the solution is acid and hydrochloric acid if the solution is strongly alkaline. To the barely alkaline solution, add 10 ml of a cold, saturated solution of sodium bicarbonate and then an excess of potassium iodide; titrate the liberated iodine at once with $0.1\,N$ arsenious acid.†

Example. — In a mixture of KIO_3 and KIO_4 weighing a grams, the iodine liberated on treatment with an acid solution of KI reacts with T milliliters of $0.1\ N\ Na_2S_2O_3$ and the same weight of sample liberates in alkaline solution only enough iodine to react with t milliliters of $0.1\ N\ As_2O_3$ solution. By comparing the equations given under **12** and **13**, it is evident that the periodate alone would react with $4\ t$ milliliters of $0.1\ N$ $Na_2S_2O_3$ in acid solution. The amount of KIO_4 and KIO_3 present will be

$$t \times 0.01150 \text{ g} = \frac{t \times 1.150}{a} \text{ per cent } KIO_4$$

$$(T - 4\ t) \times 0.003567 \text{ g} = \frac{(T - 4\ t) \times 0.3567}{a} \text{ per cent } KIO_3$$

---

* E. Müller and O. Friedberger, *Ber.*, **1902**, 2655.

† The iodine cannot be titrated in the alkaline solution with sodium thiosulfate, and the iodine in the acid solution cannot be titrated with the arsenious acid.

14. Analysis of Iodides

*Method of H. Dietz and B. M. Margosches**

$$1 \text{ l of } 0.1\,N\ KIO_3 = \frac{5\,I}{60} = 10.58 \text{ g iodine}$$

Treat the solution of the iodide with an excess of 0.1 N potassium iodate solution, make acid with sulfuric acid, add a piece of calcite as suggested by Prince,† and boil until all the iodine is expelled. Allow the solution to cool, then add an excess of potassium iodide, and titrate the iodine now liberated, which corresponds to the excess of potassium iodate used, with 0.1 N $Na_2S_2O_3$ solution.

From the equation

$$KIO_3 + 5\,KI + 6\,HCl = 6\,KCl + 3\,H_2O + 3\,I_2$$

it is evident that five-sixths of the iodine liberated comes from the iodide. If, therefore, T milliliters of 0.1 N KIO_3 solution were added and t milliliters of 0.1 N Na_2S_2O were used for titrating the excess of KIO_3, then there is present

$$(T - t) \times 0.01058 \text{ g iodine as iodide}$$

15. Determination of Copper with Potassium Iodate‡

Potassium iodate in dilute hydrochloric acid solution is reduced by potassium iodide to free iodine:

$$KIO_3 + 5\,KI + 6\,HCl = 6\,KCl + 3\,I_2 + 3\,H_2O$$

but if the solution is strongly acid with hydrochloric acid and an excess of the iodate is added, the iodine is oxidized to ICl:

$$2\,I_2 + KIO_3 + 6\,HCl = KCl + 5\,ICl + 3\,H_2O$$

and in this case the whole reaction may be expressed by the equation:

$$KIO_3 + 2\,KI + 6\,HCl = 3\,KCl + 3\,ICl + 3\,H_2O$$

The ICl is not very stable, and is at once reduced to free iodine in the presence of any oxidizable substance.

L. W. Andrew§ has shown that quite a number of reducing substances, such as free iodine, iodides, arsenites, and antimonites, can be titrated with potassium iodate very exactly, by taking advantage of the fact that when the reducing agent is present in excess, free iodine is formed which is oxidized quantitatively by more iodate, provided the proper amount of hydrochloric acid is present. Copper solutions are precipitated quantitatively by potassium thiocyanate and sulfurous acid as cuprous thiocyanate, CuSCN, and Parr|| has estimated copper quantitatively by titrating

* *Chem.-Ztg.*, **1904**, II, 1191.

† *Inaug. Dissert.*, Zürich, 1910.

‡ Jamieson, Levy, and Wells, *J. Am. Chem. Soc.*, **30**, 760 (1908).

§ *Ibid.*, **25**, 756 (1903).

|| *Ibid.*, **22**, 685 (1900).

this precipitate with permanganate. The oxidation is simpler and more accurate, however, when the titration is effected by potassium iodate or biiodate. The reaction goes through the stage in which iodine is set free, but the iodine is oxidized completely to iodine chloride upon the addition of more iodate:

(a) $10\,CuSCN + 14\,KIO_3 + 14\,HCl = 10\,CuSO_4 + 7\,I_2 + 10\,HCN + 14\,KCl + 2\,H_2O$

(b) $2\,I_2 + KIO_3 + 6\,HCl = KCl + 5\,ICl + 3\,H_2O$

and the whole reaction is

(c) $4\,CuSCN + 7\,KIO_3 + 14\,HCl = 4\,CuSO_4 + 7\,ICl + 4\,HCN + 7\,KCl + 5\,H_2O$

The potassium iodate solution is very stable and can be preserved for years if protected from evaporation. The standard solution used can be prepared by weighing out a known amount of the pure salt and dissolving to a definite volume, or the solution can be standardized against pure copper, carrying out the process as in an analysis. A convenient concentration is $\frac{1}{8}$ mole KIO_3 per liter.

Procedure. — To 0.5 g of the ore in a 200-ml flask, add 6–10 ml of strong nitric acid, and boil gently, best over a free flame, keeping the flask in constant motion and inclined at an angle of about 45°, until the larger part of the acid has been removed. If this does not completely decompose the ore, add 5 ml of strong hydrochloric acid and continue the boiling until the volume of liquid is about 2 ml. Now add gradually and carefully, best after cooling somewhat, 12 ml of 18 N sulfuric acid and continue the boiling until sulfuric acid fumes are evolved copiously. Allow to cool, add 25 ml of cold water, heat to boiling, and keep hot until the soluble sulfates have dissolved. Filter into a beaker, and wash the flask and filter thoroughly with cold water.* Nearly neutralize the filtrate with ammonia and add 10–15 ml of strong sulfur dioxide water. Heat just to boiling and add 5–10 ml of a 10 per cent solution of ammonium thiocyanate, according to the amount of copper present. Stir thoroughly, allow the precipitate to settle for 5 or 10 minutes, filter on paper, and wash with hot water until the excess ammonium thiocyanate is removed completely.

Place the filter with its contents in a glass-stoppered bottle of about 250-ml capacity, and by means of a piece of moist filter paper transfer into the bottle any precipitate adhering to the stirring-rod and beaker. Add to the bottle about 5 ml of chloroform, 20 ml of water, and 30 ml of concentrated hydrochloric acid (the two last liquids may be mixed previously). Now run in standard potassium iodate solution, inserting the stopper and shaking vigorously between additions. A violet color appears in the chloroform, at first increasing and then diminishing, until it disappears with great sharpness. The rapidity with which the iodate

* With substances containing appreciable amounts of silver a few drops of hydrochloric acid should be added before making this filtration, but not enough to dissolve any considerable amounts of the lead sulfate or antimonic oxide that may be present.

solution may be added can be judged from the color changes of the chloroform.

To make another titration it is not necessary to wash the bottle or throw away the chloroform. Pour off two-thirds or three-fourths of the liquid in order to remove most of the pulped paper, too much of which interferes with the settling of the chloroform globules after agitation, add enough properly diluted acid to make about 50 ml, and proceed as before. In this case, where iodine monochloride is present at the outset, the chloroform becomes strongly colored with iodine as soon as the cuprous thiocyanate is added, but this makes no difference in the results of the titration.

16. Iodometric Analysis of Chromite

Principle. — The chromium of chromite, $FeCr_2O_4$, is oxidized to Na_2CrO_4 by fusion with sodium peroxide. The melt is leached with water, and the insoluble residue is dissolved in hydrochloric acid, added in slight excess. Ammonium fluoride is then added to convert Fe^{+++} into FeF_6^{---}; the former ions are reduced by hydriodic acid but the latter are unaffected. Then to the acid solution an excess of potassium iodide is added and the liberated iodine is titrated with sodium thiosulfate solution using starch as indicator.

$$2\,FeCr_2O_4 + 7\,Na_2O_2 \rightarrow 2\,NaFeO_2 + 4\,Na_2CrO_4 + 2\,Na_2O \text{ (fusion)}$$

$$\left.\begin{array}{l} NaFeO_2 + 2\,H_2O \rightarrow Na^+ + \mathbf{Fe(OH)_3} + OH^- \\ 2\,Na_2O_2 + 2\,H_2O \rightarrow 4\,Na^+ + 4\,OH^- + O_2 \end{array}\right\}\text{(water added)}$$

$$2\,CrO_4^{--} + 2\,H^+ \rightarrow Cr_2O_7^{-} + :$$

$$Fe^{+++} + 6\,F^- \rightarrow FeF_6^{---} \text{ (fluoride added)}$$

$$Cr_2O_7^{--} + 6\,I^- + 14\,H^+ \rightarrow 2\,Cr^{+++} + 3\,I_2 + 7\,H_2O \text{ (iodide added)}$$

$$I_2 + 2\,S_2O_3^{--} \rightarrow 2\,I^- + S_4O_6^{--} \text{ (titration)}$$

From these equations, it is evident that the milli-equivalent weight of chromium is the atomic weight divided by 3000 as in the analysis with potassium dichromate (p. 593).

For the fusion, an iron crucible of about 25-ml capacity is commonly used. A nickel crucible is attacked less by the peroxide fusion and the presence of nickel has been found advantageous for the decomposition of the excess peroxide, but it is usually necessary to filter the solution after making it acid when a nickel crucible is used and it costs considerably more than an iron one. A porcelain crucible has also been recommended, but this again is more expensive than the iron. The fusion can also be carried out in a test-tube.

Procedure. — Weigh out 0.3–0.4 g of chromite and fuse with sodium peroxide exactly as described on p. 592. Continue as directed there down to the point where the solution is made acid. Then, instead of using sulfuric acid, add hydrochloric acid until all the hydrated ferric oxide has dissolved. Use 1 ml of concentrated hydrochloric acid in excess for each 100 ml of solution. Add 2 g of ammonium fluoride, more if necessary, until a small drop of the solution will give no test for

Fe^{+++} with potassium ferrocyanide solution on the spot plate. Add 3 g of potassium iodide, wait 3 minutes, and then titrate with sodium thiosulfate solution. Add starch solution toward the last.

17. Analysis of Soluble Chromates

A concentrated, acid solution of potassium iodide is treated with a weighed amount of the chromate, diluted with water, and the liberated iodine titrated. (Cf. standardization of sodium thiosulfate against potassium dichromate, p. 601.)

18. Determination of Lead Peroxide

*Method of Diehl, modified by Topf**

The analysis depends upon the fact that lead peroxide is reduced by means of potassium iodide in acetic acid solution when considerable alkali acetate is present:

$$PbO_2 + 4\ HI = PbI_2 + 2\ H_2O + I_2$$

After diluting with water the iodine is titrated with 0.1 N $Na_2S_2O_3$ solution.

Procedure. — Dissolve about 0.5 g of the substance with 1.2 g of potassium iodide and 10 g of sodium acetate in 5 ml of 5 per cent acetic acid. Dilute the solution with water to a volume of 25 ml and titrate with sodium thiosulfate.

Remark. — Moist lead peroxide reacts almost instantly on undergoing the above treatment; thoroughly dried material, on the other hand, dissolves after a few minutes provided it is finely ground. If the dry peroxide is in the form of coarse grains, however, it may be several hours before the reaction is finished, or the decomposition may be incomplete.

Furthermore, too much potassium iodide should not be used, as otherwise lead iodide will separate out. In that case add 3–5 g more of sodium acetate and a few milliliters of water. Shake until the lead iodide has dissolved completely, and then dilute to a volume of 25 ml. The solution must remain perfectly clear and there should not be a trace of lead iodide precipitate.

This excellent method may also be used for the analysis of minium (red lead) or pyrolusite.

19. Determination of Ozone in Ozonized Oxygen

$$1\ \text{l of } 0.1\ N\ Na_2S_2O_3 = \frac{O_3}{20} = 2.4\ \text{g } O_3$$

(a) Schönbein's Method

The most accurate method for estimating ozone consists in allowing the ozonized oxygen to act upon potassium iodide solution whereby free iodine is formed:

$$2\ KI + O_3 + H_2O = 2\ KOH + I_2 + O_2$$

* Diehl, *Dingl. polyt. J.*, **246**, 196, and Topf, *Z. anal. Chem.*, **26**, 296 (1887).

and the iodine may be titrated, after acidifying the solution with dilute sulfuric acid, by means of 0.1 *N* sodium thiosulfate.

It makes a difference, however, whether the ozone reacts with a *neutral* or with an *acid* solution. In the latter case far too much iodine is liberated, although in the former case exactly the right amount is set free. Sir B. C. Brodie* called attention to this fact in his classic researches on ozone. Brodie confirmed the results obtained in his titrations by weighing the amount of ozone used in the experiments. This work of Brodie's appears to have been forgotten,† for many other chemists have since that time attempted to work out an iodometric method for estimating ozone, some using acid solutions of potassium and iodide and some neutral solutions to absorb the gas, although for a long time it occurred to no one else that the results could be checked by weighing out a definite amount of ozone for test experiments. In 1901, however, this was done in a very simple way by R. Ladenburg and R. Quasig,‡ who were without knowledge of Brodie's work. Their method consisted in weighing a glass bulb of known capacity which was provided with glass stopcocks, filling it with oxygen, and then weighing. The oxygen was then replaced by ozone, so that *the gain in weight multiplied by* 3 *represented the amount of ozone present.*

In order, now, to titrate the ozone, Ladenburg and Quasig expelled the gas from the bulb by distilled water, and conducted it slowly through a *neutral* solution of potassium iodide which was subsequently treated with an equivalent amount of sulfuric acid and the liberated iodine titrated with *N* sodium thiosulfate.

The results of Ladenburg and Quasig have been carefully tested in the author's laboratory§ and the method improved somewhat by absorbing the ozonized oxygen by potassium iodide solution in the glass bulb itself rather than expelling the gas from the bulb and passing it into the iodide solution.

The estimation of ozone by weighing is a much too round-about process to permit a practical application, particularly on account of the fact that the measurement and weighing of the gas must take place in a room at constant temperature, a condition which cannot in many cases be readily fulfilled. Consequently the volumetric titration of the gas is far more practical.

Procedure. — Procure a glass bulb of about 300–400 ml capacity, of the form shown in Fig. 117, and determine its volume accurately by weighing it empty and then fill with water, applying the correction for temperature as described on pp. 461 *et seq.* Connect the bulb with a gas delivery tube, making use of Babo flanged joints (Fig. 117, *c* and *d*) pressing them together by means of a steel clamp, lined with cork (Fig. 118). Connect the delivery tube with the supply of ozone and oxygen, and replace the water in the bulb with the gas. During the filling of the bulb, but little of the ozone is absorbed by the water. When the tube is filled, close the lower stopcock first and the upper one a few seconds later. Then disconnect the bulb with the gas delivery tube, invert, open the upper stopcock quickly for an instant to establish atmospheric

* *Phil. Trans.*, **162**, 435–484 (1872).

† Luther and Inglis, *Z. physik. Chem.*, **48**, 208 (1903).

‡ *Ber.*, **34**, 1184 (1901).

§ Treadwell and Anneler, *Z. anorg. Chem.*, **48**, 86 (1905).

pressure in the bulb, and connect by means of rubber tubing with the gas reservoir N which is filled with $2N$ potassium iodide solution (Fig. 119). Allow the air imprisoned in the rubber tubing to escape through the three-way stopcock b, and after properly setting the cock, introduce 20–30 ml of the iodide solution into the bulb. Finally

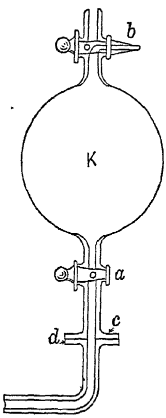

FIG. 117.

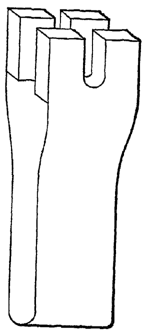
FIG. 118.

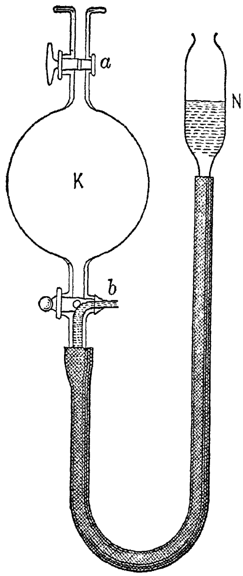

FIG. 119.

close the stopcock b and disconnect the rubber tubing. Shake the contents of the bulb vigorously and allow to stand for half an hour; at the end of this time the absorption of the ozone will be complete.

Place an Erlenmeyer flask under the stopcock b; open this and immediately afterwards the upper stopcock also. Wash out the bulb first by introducing some potassium iodide solution through a and finally with pure water. Make the contents of the flask acid with dilute sulfuric acid and titrate the liberated iodine with $0.1\,N$ sodium thiosulfate.

The computation takes place as follows: Assume the bulb to hold V milliliters; the weight of ozone found by titration $= p$ grams; the temperature $= t°$, the barometer reading $= B$ millimeters, and the tension of water vapor $= w$.

The volume of the bulb at 0° and 760 mm pressure is

$$V_0 = \frac{V(B - w)\,273}{760\,(273 + t)}$$

When filled with oxygen this would weigh:

$$\frac{0.032\ V_0}{22.41}\ \text{grams}$$

Therefore the weight of oxygen and ozone in the bulb is

$$\frac{0.032\ V_0}{22.41} + \frac{p}{3}$$

and the percentage of ozone in the mixture is

$$\frac{100\ p}{\frac{0.032\ V_0}{22.41} + \frac{p}{3}} = \frac{6720\ p}{0.096\ V_0 + 22.41\ p} = \text{per cent ozone}$$

*(b) Method of Soret-Thenard**

Ozone is absorbed quantitatively by means of sodium arsenite solution in accordance with the following equation:

$$Na_2HAsO_3 + O_3 = Na_2HAsO_4 + O_2$$

although A. Ladenburg† finds that the absorption takes place much more slowly than by means of potassium iodide. When, therefore, the ozone is passed through the arsenite solution, there is danger of getting too low results. If the absorption takes place in a glass bulb however, the results are good.

Ozone is also absorbed by alkali bisulfite‡ solutions and may be estimated in this way, by titrating the excess of bisulfite with iodine. Ladenburg,§ however, has shown that the method is not as accurate as the potassium iodide one, so that it will not be considered further here.

20. Determination of Hydrogen Peroxide. Kingzett's Method‖

1 l of 0.1 N $Na_2S_2O_3$ solution $\frac{H_2O_2}{20} = 1.7008$ g H_2O_2

The hydrogen peroxide solution is diluted until its H_2O_2 content corresponds to about 0.6 per cent by weight, and of this solution 10 ml are used in the analysis.

Procedure. — Place about 2 g of potassium iodide in an Erlenmeyer flask and dissolve in 200 ml of water. Add 30 ml of 18 N sulfuric acid, and then, with constant stirring, introduce 10 ml of the hydrogen

* *Compt. rend.*, **38**, 445 (1854), **75**, 174 (1872).

† *Ber.*, **36**, 115 (1903).

‡ Neutral alkali sulfite is not suitable here, because it is not oxidized quickly by pure oxygen alone.

§ *Loc. cit.*

‖ *J. Chem. Soc.*, **1880**, 792.

peroxide solution from a pipet. After standing 5 minutes, titrate the iodine liberated with 0.1 N thiosulfate solution.

$$H_2O_2 + 2\,KI + H_2SO_4 = K_2SO_4 + 2\,H_2O + I_2$$

Remark. — This method is rather better than that described on p. 570 because the titration can take place in the presence of glycerol, salicylic acid, etc., which are sometimes used as preservatives in commercial hydrogen peroxide preparations. These substances will render the results obtained by the permanganate titration less accurate.

21. Determination of Iron

$$1\ l \text{ of } 0.1\,N\ Na_2S_2O_3 \text{ solution} = \frac{Fe}{10} = 5.584 \text{ g Fe}$$

This method was first proposed by Carl Mohr* and is based upon the following reaction:

$$2\,FeCl_3 + 2\,HI \rightleftarrows 2\,HCl + 2\,FeCl_2 + I_2$$

As the reaction is reversible, it is necessary to have an excess of hydriodic acid present in order that it may take place quantitatively in the direction from left to right.

When carried out in the presence of air, a very little of the hydriodic acid is probably oxidized by the air, but in the following procedure this error is counter-balanced almost exactly by the fact that the reduction of the iron is not quite complete. If sulfuric acid is present, higher concentrations of both acid and iodide are required and the end point is less stable.

Procedure. — To about 30 ml of ferric chloride solution in a 200-ml Erlenmeyer flask containing 0.1–0.15 g of iron and 0.25–25 milliequivalents of hydrochloric acid, add 3 g of solid potassium iodide, stopper the flask, and allow to stand for 5 minutes. Dilute to about 100 ml and titrate with 0.1 N thiosulfate solution, adding starch solution toward the last.

22. Determination of Copper

$$1\ l \text{ of } 0.1\,N\ Na_2S_2O_3 \text{ solution} = \frac{Cu}{10} = 6.357 \text{ g Cu}$$

Principle. — If a solution of a cupric salt at a suitable concentration is treated with an excess of potassium iodide, all the copper is precipitated as cuprous iodide, and there is liberated one atom of iodine for each atom of copper present, $2\,Cu^{++} + 4\,I^- \rightarrow Cu_2I_2 + I_2$. The iodine is titrated with sodium thiosulfate solution. The method was studied by Gooch and Heath,† who found that the quantity of potassium iodide used, the concentration of the solution, and the quantity of acid present are three factors which must be taken into consideration. In a volume of 50 ml

* *Ann. Chem. Pharm.*, **105**, 53. Cf. Kolthoff, *Pharm. Weekblad*, 58, 1510 (1921); Böttger and Böttger, *Z. anal. Chem.*, **70**, 214; Grey, *J. Chem. Soc.*, **1929**, 35; Swift, *J. Am. Chem. Soc.*, **51**, 2682 (1929).

† F. A. Gooch and F. H. Heath, *Am. J. Sci.*, **4**, 25, 67; F. H. Heath, *ibid.*, 25, 153.

an excess of 0.6–1.0 g of potassium iodide is sufficient to cause the complete precipitation of 0.0020 g of copper, but in a volume of 100 ml an excess of 3–5 g is desirable. In general, the more dilute the solution, the greater the quantity of potassium iodide required. A larger excess of potassium iodide does no harm.

A little free acid does no harm, but not more than 2 ml of concentrated mineral acid may be present in 50 ml of solution.

If an appreciable amount of arsenic is present, mineral acids must not be present on account of their tendency to bring about the reduction of the higher salts of arsenic and antimony when an excess of potassium iodide is used. Obviously the solution must not contain any other oxidizing agent.

Two procedures will be given for the determination of copper in an ore. In the first method, the sample is dissolved in nitric acid, or aqua regia, and the solution is evaporated with sulfuric acid to form insoluble lead sulfate. The insoluble residue together with lead sulfate is filtered off and the solution boiled with aluminum which precipitates copper and reduces ferric iron. The copper is filtered off and dissolved in nitric acid; after this the procedure is practically the same as in the standardization against copper wire. The purpose of precipitating the copper with aluminum is to separate it from iron which, in the ferric condition, is reduced by potassium iodide.

This method is accurate but long. Low himself recommended a shorter procedure for ordinary work. In the short method recommended by him, the solution was evaporated to dryness and the dry residue was leached with strong ammonia solution which dissolved out the cupric salt as blue cupric ammonia complex and left the iron behind. After the solution was made acid with acetic acid, it was treated with potassium iodide and the liberated iodine titrated with thiosulfate. After some practice with this short method good results can be obtained but if the residue has become baked, often some of the copper does not dissolve, whereas if the evaporation has taken place during constant rotation of the flask while being heated over a free flame and the heating is stopped as soon as the residue is dry, the extraction of all the copper is possible if sufficient salt, such as potassium chloride, is present.

It has been found, however, that it is possible to avoid the separation of the copper from the iron if some substance, such as fluoride, is added to convert the ferric cations into a slightly ionized complex. Then, if the solution is buffered to give the proper hydrogen-ion concentration, the solution can be titrated just as if no iron were present. The method of Bartholow Park,* which will be described after that of Haën-Low, is based upon this principle.

(*a*) Method of Haën†-Low‡

Procedure. — To 0.25–0.50 g of fine ore weighed into a 250-ml Erlenmeyer flask, add 6 ml of 16 *N* HNO_3, and boil gently until nearly dry. Add 5 ml of 12 *N* HCl and heat again. As soon as the incrusted matter has dissolved add 12 ml of 18 *N* H_2SO_4 and heat until the acid fumes freely. Cool and add 25 ml of water. Then heat until any anhydrous ferric sulfate is dissolved, and filter to remove insoluble sulfates and silica. Wash the flask and filter paper with hot water until the volume

* *Ind. Eng. Chem., Anal. Ed.*, **3**, 77 (1931).

† *Ann. Chem. Pharm.*, **91**, 237 (1854).

‡ Technical Methods of Ore Analysis.

of the filtrate amounts to about 75 ml, receiving it in a 150-ml beaker. Take a strip of aluminum, about 2.5 cm wide and 14 cm long, bend it into a triangle, and place it in the beaker resting on its edge. Cover the beaker and boil gently for 7–10 minutes, which will be sufficient to precipitate all the copper, provided the solution does not much exceed 75 ml. Avoid boiling to a very small volume. The aluminum should now appear clean, the copper being detached or loosely adhering. Remove from the heat and wash down the cover and sides of the beaker with hydrogen sulfide water. This will prevent oxidation and will also serve to precipitate the last traces of copper. If the hydrogen sulfide shows that there was more than a very little copper remaining in solution, it is best to dilute the solution to 75 ml again and to boil a short time longer. This will coagulate the sulfide. Finally, decant through a filter and then, without delay, transfer the precipitate to the filter with the aid of a stream of hydrogen sulfide water from a wash-bottle. Let the strip of aluminum remain in the beaker, but wash it as clean as possible with the hydrogen sulfide water. Wash the filter and precipitate at least 6 times with this hydrogen sulfide water, but take care not to let the filter remain empty for any length of time. Moist copper sulfide oxidizes very rapidly when in contact with the air with the formation of a little copper sulfate, which will dissolve and pass through the filter only to precipitate again when it comes in contact with the filtrate containing hydrogen sulfide.

Now place the original clean flask under the funnel, perforate the filter and rinse the precipitate into the flask with hot water, using as little as possible. Lift the fold of the filter and rinse down any precipitate found beneath the fold. Using a small pipet, allow 5 ml of strong nitric acid to run over the aluminum in the beaker and pour it from the beaker through the filter into the flask, but do not wash the beaker or filter at this stage. Remove the flask and replace it with the beaker. Heat the contents of the flask to dissolve the copper and expel the red fumes, then again place the flask under the funnel. Now pour over the filter 5 ml or more of bromine water, using enough to impart a strong color to the solution in the flask. Next wash the beaker and aluminum, pouring the washings through the filter. Finally wash the filter 6 times with hot water. Boil till the solution is reduced to about 25 ml, cool somewhat, and add a slight excess of strong ammonia (about 7 ml). Boil off the excess of ammonia, add an excess of acetic acid, and boil a minute longer. Cool to room temperature, add 3 g of potassium iodide, and titrate with sodium thiosulfate solution, adding starch toward the last.

(*b*) Method of Park

Dissolve the sample exactly as described in the above method of Haën-Low and continue exactly as described there but receive the filtrate from the lead sulfate precipitate in a 250-ml Erlenmeyer flask. Concentrate to about 30 ml, cool, and add ammonium hydroxide until the greater part of any iron present is precipitated or the solution smells faintly of ammonia after blowing away the vapors from the top of the flask. Be careful to avoid an excess of ammonia. Heat if necessary to remove excess ammonia. Add 2 g of ammonium bifluoride, weighed to the nearest centigram, and 1 g of potassium biphthalate, also weighed to the nearest centigram. Add approximately 3 g of potassium iodide and titrate at once with thiosulfate solution, adding starch toward the last.

Under the above conditions the p_H of the solution is about 4 and antimony or arsenic are not reduced by the iodide. Ferric iron is not reduced because it is present for the most part as FeF_6^{---} anions.

23. Analysis of Arsenious Acid

(*a*) The titration can take place in exactly the same way as in the standardization of 0.1 N iodine solution (see p. 603).

(*b*) Titration of Arsenious Acid with Potassium Bromate

$$1 \text{ l of } 0.1\,N\ KBrO_3 = \frac{KBrO_3}{60} = 2.784 \text{ g } KBrO_3 = 4.948 \text{ g } As_2O_3$$

Principle. — If a hydrochloric acid solution of arsenious acid is treated with potassium bromate, the arsenic is completely oxidized to arsenate. As soon as all the arsenic is oxidized, the next drop of potassium bromate solution causes separation of bromine.

$$3\,Na_2HAsO_3 + KBrO_3 + 6\,HCl = 6\,NaCl + KBr + 3\,H_3AsO_4$$
$$KBrO_3 + 5\,KBr + 6\,HCl = 6\,KCl + 3\,H_2O + 3\,Br_2$$

If the solution contains methyl orange it will show an acid reaction as long as arsenic is present, but free bromine destroys the indicator and the solution becomes colorless at the end point.

24. Determination of Antimony Trioxide Compounds

$$1 \text{ liter of } 0.1\,N \text{ iodine solution} = \frac{Sb_2O_3}{40} \quad 7.289 \text{ g. } Sb_2O_3 = 6.089 \text{ g. } Sb$$

The titration is carried out exactly as in the case of arsenious acid (cf. p. 603) except that tartaric acid, or Rochelle salt, must be added to the solution in order to prevent the precipitation of antimonous acid, or antimony oxychloride, as a result of hydrolysis.

Examples:

(a) *Determination of Antimony in Tartar Emetic*

If an aqueous solution of tartar emetic is treated with iodine in the presence of starch, the first few drops of reagent will impart a permanent blue color to the solution. If, however, a little sodium bicarbonate is added to the solution, the trivalent antimony is oxidized quantitatively to the quinquevalent condition.

$$K(SbO)C_4H_4O_6 + 6\,NaHCO_3 + I_2 = Na_3SbO_4 + 2\,NaI + KNaC_4H_4O_6 + 3\,H_2O + 6\,CO_2$$

$$1 \text{ liter of } 0.1\,N \text{ iodine solution} = \frac{K(SbO)C_4H_4O_6 + \frac{1}{2}\,H_2O}{20} = 16.70 \text{ g}$$

Dissolve 8.350 g. of tartar emetic in water, dilute the solution to exactly 500 ml. and mix well. Of this solution, transfer 20 ml. with a pipet into 100 ml. of water containing 0.5 g. of sodium bicarbonate. Titrate with 0.1 N iodine solution, using starch as an indicator.

(b) *Determination of Antimony in Stibnite*

1 ml of normal iodine solution = 0.06089 g Sb

Principle. — Stibnite, Sb_2S_3, dissolves in 12 N normal hydrochloric acid with evolution of hydrogen sulfide.

$$Sb_2S_3 + 8\,HCl \rightarrow 2\,HSbCl_4 + 3\,H_2S \uparrow$$

After the hydrogen sulfide has been removed, tartaric acid is added to form the antimonyl tartrate ion which is so stable that it prevents the hydrolysis of the antimony salt upon dilution:

$$SbCl_4^- + H_2C_4H_4O_6 + H_2O \rightarrow H(SbO)C_4H_4O_6 + 3\,H^+ + 4\,Cl^-$$

The final titration takes place as follows:

$$H(SbO)C_4H_4O_6 + I_2 + 2\,HCO_3^- \rightarrow H(SbO_2)C_4H_4O_6 + 2\,I^- + H_2O + 2\,CO_2 \uparrow$$

Weigh out 0.2–0.3 g of stibnite into a 150-ml beaker, cover with a watch glass, and add 10 ml of concentrated hydrochloric acid. Allow the acid to act in the cold for 10 minutes, add 0.3 g of solid potassium chloride, and heat gently on the water-bath for 15 minutes to complete the attack and expel hydrogen sulfide. Take care not to allow the liquid to evaporate sufficiently to expose any part of the bottom of the beaker. There is usually a silicious residue, insoluble in hydrochloric acid.

Remove the beaker from the water-bath, cool to room temperature, and add a solution of 3 g of tartaric acid which has been dissolved by heating in a test-tube with 5 ml of water and cooled under running water. Mix well by rotating the contents of the beaker. Slowly add water, while stirring, to a volume of about 100 ml.

Pour this solution slowly, while stirring, into a 600-ml beaker containing 10 g of sodium carbonate dissolved in 200 ml of cold water. This serves to neutralize the acid and provide sufficient sodium bicarbonate to keep the solution neutral during the iodine titration. Wash down the

sides of the beaker, add starch paste, and titrate with iodine to the appearance of a permanent blue.

If a fugitive end point is obtained, SbOCl has been precipitated or not enough sodium bicarbonate is present.

Remarks. — Antimony chloride is volatile with steam from its concentrated solutions, but the heating on the water-bath can be carried out, without fear of losing antimony, provided most of the acid is not allowed to evaporate and KCl is present to form less volatile $KSbCl_4$. This heating serves to remove all the hydrogen sulfide which would otherwise precipitate the antimony as trisulfide upon diluting the solution. If insufficient tartaric acid is present, antimony oxychloride, SbOCl, precipitates, and if the solution is titrated in this condition it is impossible to obtain a permanent end point.

(c) *Titration of Antimonous Acid with Potassium Bromate**

$$1 \text{ l of } N\ KBrO_3 = \frac{Sb_2O_3}{40} = 7.289 \text{ g } Sb_2O_3 \text{ or } 6.089 \text{ g Sb}$$

The procedure is the same as that described on p. 627. Enough hydrochloric acid must be used to prevent the precipitation of SbOCl.

25. Determination of Antimony Pentoxide Compounds (A. Weller)†

By heating a quinquevalent antimony compound with concentrated hydrochloric acid and potassium iodide in the Bunsen apparatus (Fig. 114, p. 600), the antimonic acid is reduced to antimonous acid with separation of iodine:

$$Sb_2O_5 + 4\,HI = Sb_2O_3 + 2\,H_2O + 2\,I_2$$

The iodine is distilled over into potassium iodide solution and titrated with 0.1 N $Na_2S_2O_3$ solution. The results are a little low.

26. Determination of Tin with Potassium Bromate‡

$$1 \text{ l of } 0.1\ N\ KBrO_3 = \frac{Sn}{20} = 5.935 \text{ g Sn}$$

Place 20 ml of faintly acid stannous or stannic solution (about 6 g of tin per liter) in a 200-ml flask, add 0.15 g of aluminum wire in short pieces, and allow the reaction to proceed in the cold until all the tin is precipitated. Add 30 ml of concentrated hydrochloric acid and 20 ml of water, and stopper the flask with a Bunsen valve (p. 548). Heat gently till all the tin has dissolved. Cool and titrate with 0.1 N potassium

* Method of H. Zschokke. Cf. Fiechter and Mueller, *Chem. Ztg.*, **37**, 309 (1913).

† *Ann. Chem. Pharm.*, **213**, 364.

‡ St. Györy, *Z. anal. Chem.*, **32**, 415 (1893).

bromate solution (2.784 g per liter) until a permanent yellow color is obtained.

$$- BrO_3^- + 6\,H^+ = 3\,H_2O + Br^- + 3$$

$$BrO_3^- + 5\,Br^- + 6\,H^+ = 3\,Br_2 + 3\,H_2O$$

Remark. — Boller obtained low results when testing pure tin. He has improved the method by adding a slight excess of bromate, then some potassium iodide, and finally titrating with sodium thiosulfate. The results are about 1 per cent too low if air is present in the solution. Boller proceeds as follows:

Place 100 ml of $7\,N$ hydrochloric acid in the 500-ml flask shown in Fig. 120, and boil 5 minutes to expel air, with stopcock A open and B closed. Remove the flame and quickly introduce the weighed sample of metallic tin and a little piece of calcite to furnish carbon dioxide gas. Replace the top piece and, with B open, boil gently until all the tin is dissolved. Then close B and cool the contents of the flask with cold water. This produces a partial vacuum in the flask.

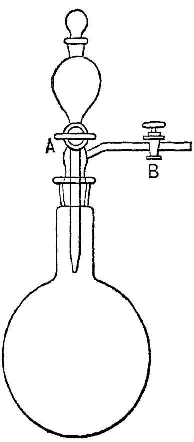

FIG. 120.

While the tin is dissolving prepare a mixture of 50 ml of $0.1\,N$ $KBrO_3$ solution, 1 g of potassium bromide, and a little water. Boil 5 minutes to expel air. Pour this solution into the funnel of the above-mentioned flask and allow it to flow into the stannous solution by carefully opening the stopcock A. The stannous chloride is oxidized instantly to stannic salt. Rinse out the contents of the funnel with boiled water, add 10 ml of 5 per cent potassium iodide solution, and titrate with $0.1\,N$ thiosulfate.

The tin determination as originally given by Zschokke gives good results if the bromate solution is standardized against tin in the same way that the analysis is made.

27. Determination of Hydrogen Sulfide

$$1\ \text{l of } 0.1\,N\ Na_2S_2O_3 \text{ solution} = \frac{H_2S}{20} = 1.704\ \text{g}\ H_2S$$

If a solution of hydrogen sulfide is treated with iodine, it is oxidized with separation of sulfur: $H_2S + I_2 = 2\,HI + S$.

For the determination of the amount of the gas present in hydrogen sulfide water, transfer a measured amount by means of a pipet to a

known volume of 0.1 N iodine solution and titrate the excess of the latter with thiosulfate solution.*

If the amount of hydrogen sulfide present is not very large, correct results are obtained without difficulty. With considerable hydrogen sulfide, on the other hand, the deposited sulfur is likely to enclose some of the iodine solution, as shown by its brown color; this iodine escapes the titration with thiosulfate. In such a case, remove the film of sulfur floating on the surface of the liquid with a glass rod after the completion of the thiosulfate titration, transfer it to a glass-stoppered cylinder, and shake with 1–2 ml of carbon bisulfide. The latter dissolves the iodine with a violet color and the color can be discharged with sodium thiosulfate solution.† In this way the total amount of the iodine that remains can be titrated.

Remark. — This method can be used to advantage for determining the sulfur present in soluble sulfides.

Determination of Hydrogen Sulfide in Mineral Waters

Place a measured amount of 0.01 N iodine solution and 2 g of potassium iodide in a tall liter cylinder, add 1 l of the water to be analyzed, and, after thoroughly shaking, titrate the excess of the iodine with 0.01 N thiosulfate. The standardization of the iodine solution used is accomplished by measuring off 10 ml of the solution, adding 2 g of potassium iodide, diluting to 1 l with boiled water, and titrating with 0.01 N thiosulfate solution.

Remark. — The hydrogen sulfide in a water is not always present as free gas but may be present as hydrosulfide, *i.e.*, as HS^- anions. The mineral water will also contain free carbonic acid and HCO_3^- anions. According to the mass-action law:

$$(1)\quad \frac{[H^+] \times [HS^-]}{[H_2S]} = 0.91 \times 10^{-7} \qquad \text{and} \qquad (2)\quad \frac{\qquad}{[H_2CO_3]}$$

Since the two equilibria are both satisfied in the solution, the hydrogen-ion concentrated is the same in each expression. $[H^+] = \frac{0.91 \times 10^{-7} \times [H_2S]}{[HS^-]}$, and in-

* Correct results cannot be obtained by titrating directly with iodine; cf. O. Brunck, *Z. anal. Chem.*, **45**, 541 (1906).

† The separation of the sulfur into a coherent film can be prevented by sufficiently diluting the solution with boiled water. O. Brunck (*Z. anal. Chem.*, **45**, 541) therefore, recommends using 0.01 N iodine instead of 0.1 N solution, and this is certainly advisable with small quantities of hydrogen sulfide as, for example, in a mineral water. On the other hand, when a relatively large volume of hydrogen sulfide is liberated from a sulfide by means of acid it is advisable to use 0.1 N iodine, as otherwise the volume of solution will be too large unless a very small weight of substance is used in the analysis.

serting this value in equation (2) we have

(3)

In all these equations the symbols in brackets represent moles per liter of the substance.

With the aid of equation (3) it is possible to compute the quantity of free hydrogen sulfide present in a sample of mineral provided a complete analysis of the water has been made.

Let C = the total millimoles per liter of non-ionized H_2CO_3 and HCO_3^-, let S = the total millimoles per liter of HS^- and non-ionized H_2S, and let d = the difference between the total milli-equivalents of cations per liter and of the anions with the exception of HCO_3^- and HS^-. Then $d = [HS^-] + [HCO_3^-]$, $S = [HS^- + H_2S]$ and $C = d + [H_2CO_3] - [HS^-]$.

From this it follows:

$$[HS^-] = S - [H_2S]$$
$$[HCO_3^-] = d - [HS^-] = d - S + [H_2S]$$
$$[H_2CO_3] = C - d + [HS^-] = C - d + S - [H_2S]$$

Substituting these values in equation (3) we get:

$$\frac{S - [H_2S]}{[H_2S]} = 0.3\,\frac{d - S + [H_2S]}{C - d + S -}$$

and by solving the equation

$$(4)\quad [H_2S] = \frac{(1.7S - C - 0.7d) \pm \sqrt{(1.7S + C - 0.7d)^2 - 2.8S(S + C - d)}}{1.4}$$

= millimoles of free H_2S per liter.

This value multiplied by 34.09 gives the weight of free H_2S in grams.

28. Analysis of Alkali Sulfides

$$1\ \text{l of } 0.1\ N \text{ iodine solution} = \frac{R_2S}{20} \text{ or } \frac{S}{20} = 1.603 \text{ g S}$$

Allow a measured volume of the alkali sulfide solution to run slowly, with constant stirring, into 300–400 ml of water, an excess of iodine and hydrochloric acid.* Titrate the excess of iodine with sodium thiosulfate solution.

Remark. — It does not work to titrate directly with the iodine solution.

29. Determination of Alkali Sulfides with Potassium Bromate†

$$1\ \text{l of } 0.1\ N\ KBrO_3 = \frac{H_2S}{80} = 0.4260 \text{ g } H_2S$$

Place the measured sample of solution in the liter bottle shown in Fig. 121, which is provided with a ground-glass stopper carrying a drop-

* To determine how much acid is necessary, titrate a trial sample with methyl orange as indicator with 6 N hydrochloric acid.

† Treadwell and Mayr, *Z. anorg. Chem.*, **92**, 127 (1915).

ping funnel. Add a considerable excess of 0.1 N potassium bromate solution and 3–4 g of potassium bromide. Evacuate the bottle with a water-suction pump and close the stopcock. Pour hydrochloric acid in the funnel and allow it to flow into the bottle by carefully opening the stopcock. When the solution is distinctly acid, close the stopcock and shake the contents of the bottle. To effect a good oxidation, the solution should contain 25 per cent of concentrated hydrochloric acid by volume. At first the solution assumes a brown color, then the color fades but should remain distinctly yellow. A slight turbidity of sulfur disappears in 10–15 minutes, being oxidized to sulfuric acid.

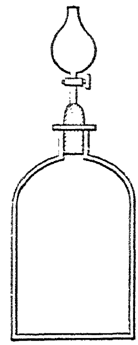

Fig. 121.

When the solution is perfectly clear, wash out the funnel with a little water but avoid letting air enter. Add 2–3 g of potassium iodide dissolved in a little water and shake. Rinse out the funnel and titrate with sodium thiosulfate solution.

If T is the volume of 0.1 N bromate solution used and t the volume of 0.1 N thiosulfate, then $(T - t)$ 0.0004260 g H_2S is present.

This method is a little more complicated than direct titration with iodine, but as the oxidation of the sulfur is from sulfide to sulfate, 4 times as much oxidizing agent is required. The method is suitable for the titration of hydrogen sulfide in the presence of thiocyanate.

30. Titration of Alkali Sulfide in the Presence of Alkali Thiocyanate

The reactions involved in the method are illustrated by the following equations:

$$(a) \quad \begin{array}{l} H_2S + 4\,H_2O + 4\,Br_2 = 8\,HBr + H_2SO_4 \\ HCNS + 4\,H_2O + 3\,Br_2 = H_2SO_4 + HCN + 6\,HBr \end{array}$$

$$(b) \quad H_2S + I_2 = 2\,HI + S$$

In one sample determine the total sulfur content by the method just described, and in another sample determine the sulfide iodometrically according to **28**, p. 632. If the total 0.1 N potassium bromate solution used was T milliliters and t milliliters of thiosulfate were used for titrating the excess and t_1 milliliters of 0.1 N iodine solution were used for the direct titration of sulfide in the same weight of substance, a grams, then

$$\frac{[(T - t) - 4\,t_1]\,0.0968}{} = \text{pe}$$

and $$\times\,0.1603 = \text{per cent S (as sulfide)}$$

31. Analysis of Mixtures of Alkali Sulfide, Alkali Hydrosulfide and Hydrogen Sulfide

$$1\ \text{l of } 0.1\ N \text{ iodine solution} = \begin{cases} 1.704\ \text{g } H_2S \\ 2.803\ \text{g NaHS} \\ 3.903\ \text{g } Na_2S \end{cases}$$

Principle. — If a solution of alkali sulfide and alkali hydrosulfide is treated with an acid solution of iodine, the following reactions take place:

$$(a)\quad Na_2S + 2\,HCl = 2\,NaCl + H_2S$$
$$(b)\quad NaSH + HCl = NaCl + H_2S$$
$$(c)\quad H_2S + I_2 = 2\,HI + S$$

Hydrogen sulfide is a very weak acid, without effect upon phenolphthalein indicator. After oxidation, the hydrogen sulfide is replaced by the strong mineral acid, hydriodic acid.

It is evident from the above equations that in the case of the sulfide, the quantity of hydriodic acid formed by the oxidation of the hydrogen sulfide is equivalent to the quantity of hydrochloric acid required to decompose the sulfide. In the case of the hydrosulfide, however, which is the acid salt of hydrogen sulfide, the quantity of hydriodic acid formed is equivalent to twice the quantity of hydrochloric acid required to decompose the hydrosulfide.

By determining the quantity of acid or base present at the start the acidity at the end of the analysis, and the quantity of iodine used in oxidizing the sulfide to free sulfur, one can distinguish between the following possibilities, in which it is assumed that any strong acid present is hydrochloric acid and any base is sodium hydroxide. The reasoning applies, of course, to cases where other strong acids or other bases are present. The solution may contain

(1) Sodium hydroxide, NaOH, and sodium sulfide, Na_2S.
(2) Sodium sulfide alone.
(3) Sodium sulfide, Na_2S, and sodium hydrosulfide, NaHS.
(4) Sodium hydrosulfide alone.
(5) Sodium hydrosulfide, NaHS, and hydrogen sulfide, H_2S.
(6) Hydrogen sulfide alone.
(7) Hydrogen sulfide, H_2S, and hydrochloric acid, HCl.

Any other possibility is excluded because sodium hydroxide and sodium hydrosulfide react to form sodium sulfide, sodium sulfide and hydrogen sulfide react to form sodium hydrosulfide, sodium hydrosulfide and hydrochloric acid react to form hydrogen sulfide. We may regard these last three reactions as taking place practically completely because there is a great difference in the ionization constants of HCl, H_2S and HS^-.

Now let us consider what will happen in the analysis of the seven mixtures just mentioned. In the analysis let us assume that a milli-equivalents of iodine solution together with b milli-equivalents of hydrochloric acid are added at the start. The excess iodine is titrated with c milli-equivalents of sodium thiosulfate, and after that d milli-equivalents of sodium hydroxide are added to make the solution neutral to phenolphthalein. From these four values, a, b, c, and d, we can easily compute the quantity of NaOH, Na_2S, NaHS, H_2S, and HCl originally present, but, as just

explained, the only possible combinations will be two neighboring compounds, NaOH and Na_2S, Na_2S and NaHS, NaHS and H_2S, H_2S and HCl.

(1) In this case, the hydrochloric acid added at the beginning of the analysis will be neutralized by both NaOH and Na_2S. The quantity of iodine required will be equivalent to the sulfide present, and, since the weak hydrogen sulfide becomes strong hydriodic acid, just as much hydriodic acid will be formed as was required of hydrochloric acid to liberate hydrogen sulfide from the sodium sulfide.

$$a - c = \text{milli-equivalents of sulfide present}$$
$$b - d = \text{milli-equivalents of NaOH}$$

The molecular weight of Na_2S divided by 2000 is the milli-equivalent weight of Na_2S.

(2) In the second case, when sodium sulfide alone is present, $b = d$ and $a - c =$ milli-equivalents of sulfide as in case (1).

(3) When sodium sulfide and sodium hydrosulfide are both present, the relations are a little more complicated. As in the previous cases, $a - c =$ the milli-equivalents of sulfide present and the milli-equivalents of sodium sulfide and of sodium hydrosulfide from the standpoint of iodometry are the molecular weight divided by 2000 in each case. The value d in this case is greater than b; $d - b =$ the milli-equivalents of NaHS present and $a - c > 2\ (d - b)$ because the milli-equivalent weight of sodium hydrosulfide from the acidimetric standpoint is one-thousandth of the molecular weight. Therefore, if we subtract from $a - c$ (the total milli-equivalents of iodine required for Na_2S and NaHS) twice the value of $d - b$, the difference will be the milli-equivalents of Na_2S present.

(4) Here $a - c = 2\ (d - b)$. The NaHS content can be computed from either $a - c$ or from $d - b$, but we must remember to divide the molecular weight of NaHS by 2000 if we wish to find the milli-equivalent from the iodometric standpoint and by 1000 if we wish to find the milli-equivalent from the acidimetric standpoint.

(5) When NaHS and H_2S are present, $a - c < 2\ (d - b)$. Here, as in every other case, the milli-equivalent of each sulfide is the molecular weight divided by 2000 from the iodometric standpoint. With respect to the HI formed by the action of iodine, the milli-equivalent weight of NaHS is the molecular weight divided by 1000, but with hydrogen sulfide it is the molecular weight divided by 2000 exactly as in the iodine titration. If we call n_1 the number of millimoles of NaHS and n_2 the millimoles of H_2S, then

$$2\,n_1 + 2\,n_2 = a - c$$
$$n_1 + 2\,n_2 = d - b$$

(6) When hydrogen sulfide alone is present

$$a - c = d - b$$

(7) When hydrogen sulfide and hydrochloric acid are present, $a - c < d - b$. From the value of $a - c$ the quantity of H_2S can be computed, and by subtracting $a - c$ from $d - b$ the milli-equivalents of HCl present are found.

In any case, therefore, all we have to do is to compare the milli-equivalents of iodine with the milli-equivalents of acid or base required to neutralize the solution after the iodine titration. Calling the former value T_1 ($a - c$ in the above notation) and the latter value T_2 ($d - b$ in the above notation), the above seven cases can be summarized as follows:

(1) In determining T_2, we find that $b > d$. The solution contains NaOH and Na_2S.
(2) $T_2 = 0$. Na_2S alone is present.
(3) $T_1 > 2\,T_2$. Na_2S and NaHS are present.
(4) $T_1 = 2\,T_2$. NaHS alone is present.
(5) $T_1 < 2\,T_2$. NaHS and H_2S are present.
(6) $T_1 = T_2$. H_2S alone is present.
(7) $T_1 < T_2$. H_2S and HCl are present.

The question naturally occurs to the student at this point as to whether such a study is of great importance. No such claim can be made. There is really no need of asking the student to carry out such an analysis in the laboratory in an elementary course of instruction. On the other hand, it is profitable for the student to try to understand these relations, for such problems do actually arise in chemical practice and, if the student understands what is meant by an equivalent weight, there is no reason why he should find great difficulty in following the above reasoning. Confusion arises from the fact that the milli-equivalent weight varies in accordance with the nature of the chemical reaction involved. The mathematical computations involve nothing more difficult than elementary algebra.

Procedure. — Dilute a known volume of 0.1 N iodine together with a known volume of 0.1 N hydrochloric acid* in a beaker to a volume of about 400 ml, and slowly add the solution containing the dissolved sulfide from a buret with constant stirring, until the mixture becomes pale yellow. Add starch indicator and titrate the excess of iodine with tenth-normal thiosulfate solution. Finally, titrate the acid in the solution with 0.1 N sodium hydroxide solution, using phenolphthalein as indicator. Calculate the results as outlined above.

32. Determination of Sulfur in Steel

Transfer 5 g of steel borings to a 250-ml flask which is fitted with a rubber stopper carrying a thistle tube that extends nearly to the bottom of the flask and a Kjeldahl distilling-bulb which ends just below the surface of the stopper (Fig. 122). This bulb acts as a splash trap. Connect the outside end of the bulb with glass tubing that reaches nearly to the bottom of a 200-ml Erlenmeyer flask. Connect the latter with a second Erlenmeyer flask. In each of the Erlenmeyer flasks place 50 ml of water and 10 ml of either of the following ammoniacal absorbents.

Ammoniacal Zinc Sulfate. — Dissolve 20 g of $ZnSO_4 \cdot 7H_2O$ in 100 ml of water and to the solution add an equal volume of concentrated ammonium hydroxide. Filter after standing over night.

Ammoniacal Cadmium Chloride. — Dissolve 12 g of $CdCl_2 \cdot 2H_2O$ in 150 ml of water and to the solution add 60 ml of concentrated ammonium hydroxide. Filter if not clear.

* Enough acid to decompose all sulfide must be present. An excess does no harm.

Pour 80 ml of 6 N HCl through the thistle tube of the evolution flask and heat so that there is a rapid and steady evolution of gas. When all the steel has dissolved boil for 30 seconds but never long enough to cause much HCl to pass over into the other flasks. The first flask should contain all the sulfur of the steel as white ZnS or as yellow CdS. The second flask is used merely to make sure that no H_2S escapes unabsorbed. Filter off the sulfide precipitate, and wash out the flask twice with dilute NH_4OH (approximately 0.5 N). Transfer the filter and precipitate to a beaker and cover with 300 ml of water. Rinse out the delivery tubing, where there is any sulfide, with 50 ml of N HCl, and add this solution to the liquid in the beaker containing the precipitate. At once add a measured volume of standard iodine solution (10 ml of 0.05 N solution is usually sufficient and should be added from a pipet), and after a few minutes titrate the excess iodine with sodium thiosulfate solution to a starch end point (see p. 601).

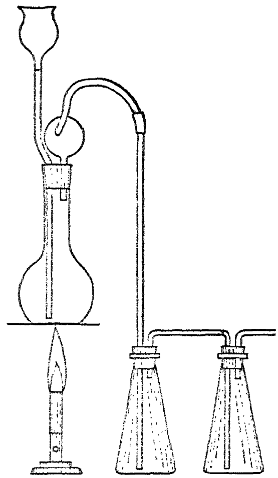

FIG. 122.

Unless the relative strengths of the two solutions have been checked recently, add 10 ml of the iodine solution from a pipet to 300 ml of water to which 5 ml of concentrated HCl has been added and titrate with thiosulfate to a starch end point.

In this analysis, the milli-equivalent weight of sulfur is 0.016 g. Standardize the solutions by any method described on pp. 599–604.

Most cast irons do not give up all their sulfur by this method of analysis. The values are nearer the truth if the sample is annealed as follows: Wrap 5 g of sample in two 11-cm filter papers so that all the metal is under at least 3 thicknesses of paper. Place in a 25-ml porcelain crucible, cover with a well-fitting lid, and heat 30–40 minutes at about 750°. Cool slowly, and transfer the charred paper and steel to the evolution flask. With high-silicon irons, heat the acid rapidly to boiling and then allow to simmer.

33. Determination of Thiosulfate in the Presence of Sulfide and Hydrosulfide

Treat a measured volume of the solution in a 200-ml measuring-flask with an excess of freshly precipitated cadmium carbonate. Shake well and dilute the liquid to the mark. Filter through a dry filter, reject the first 20 ml of filtrate, and titrate 100 ml with iodine solution.

By shaking with cadmium carbonate, the sulfide and hydrosulfide are removed and the thiosulfate remains in solution.

34. Determination of Sulfurous Acid

$$1 \text{ l of } 0.1\,N \text{ iodine solution} = \frac{SO_2}{20} = 3.203 \text{ g } SO_2$$

The determination is based upon the following reaction:

$$SO_2 + 2\,H_2O + I_2 = 2\,HI + H_2SO_4$$

the sulfurous acid being oxidized to sulfuric acid. If starch is added to a solution of sulfurous acid, and a titrated iodine solution is run into it from a buret, the blue color will not be obtained until all the sulfurous acid has been acted upon. Bunsen, however, in 1854 showed that this sensitive reaction, which was first used by Dupasquier, will take place quantitatively according to the above equation only when the solution does not contain more than 0.04 per cent by weight of SO_2. With greater concentrations uniform results are not obtained. This irregularity was ascribed to the reversibility of the reaction, so that it was suggested that the titration be performed in alkaline solution,* thus removing the hydriodic acid as fast as it is formed. But the results then obtained are still inaccurate.† Finkener,‡ on the other hand, states that correct values will be obtained if the sulfurous acid is allowed to run into the iodine solution.

J. Volhard§ has confirmed the results of Finkener and shown that the anomalous results obtained on titrating sulfurous acid with iodine are not due to the reversibility of the reaction, for the direct addition of 20 per cent sulfuric acid is without influence. The incomplete oxidation of the sulfurous acid is caused by the fact that the hydriodic acid reduces a part of the sulfurous acid to free sulfur:||

$$(1)\quad SO_2 + 4\,HI = 2\,I_2 + 2\,H_2O + S$$

* Addition of $MgCO_3$ or $NaHCO_3$ (Fordos and Gelis).

† E. Rupp, *Ber.*, **35**, 3694 (1902), states that it is possible to obtain good results by the method of Fordos and Gelis if the sulfurous acid is allowed to act for at least half an hour upon an excess of iodine in the presence of sodium bicarbonate. The solution is then titrated with sodium thiosulfate. According to E. Müller and O. Diefenthäler, however, this is theoretically incorrect, for the iodine tends to form a little hypoiodite: $I_2 + H_2O \rightleftarrows HI + HIO$, which reacts with sodium thiosulfate: $Na_2S_2O_3 + 4\,HIO + H_2O = Na_2SO_4 + H_2SO_4 + 4\,HI$.

‡ Finkener-Rose, *Quantitative Analyse*, p. 937 (1871).

§ *Ann. Chem. Pharm.*, **242**, 94.

|| If iodine solution is added slowly to a not too-dilute sulfurous acid solution, a distinct separation of sulfur is soon apparent.

If sulfurous acid, whether dilute or concentrated, is allowed to run into a solution of iodine with constant stirring, there is complete oxidation of the SO_2:

$$(2)\quad SO_2 + I_2 + 2\,H_2O = 2\,HI + H_2SO_4$$

If, on the contrary, iodine solution is run into the solution of sulfurous acid, both reactions will take place:

$$(3)\quad 3\,SO_2 + 4\,HI + 2\,H_2O = 2\,H_2SO_4 + 4\,HI^* + S$$

According to Raschig,† however, Volhard's explanation is also incorrect, for he finds that no separation of free sulfur takes place if the iodine is allowed to act upon sulfur dioxide in a *dilute* solution. Raschig believes that the error that results when iodine is added to the sulfurous acid solution is due to a loss of SO_2 by evaporation.

Correct results are always obtained if the sulfurous acid is added slowly, with constant stirring, to the iodine solution until the latter is decolorized.

In the analysis of sulfites, add the sulfite solution from a buret to the solution of iodine and hydrochloric acid.

35. Determination of Formaldehyde (Formalin). Method of G. Romijn‡

$$1\text{ l of }0.1\,N\text{ iodine solution} = \frac{HCHO}{20} = 15.01\text{ g formaldehyde}$$

Principle. — Formaldehyde is quantitatively oxidized to formic acid by remaining in contact with iodine for a short time in alkaline solution:

$$HCHO + H_2O + I_2 = 2\,HI + HCOOH$$

Procedure. — The aqueous solution of formaldehyde, known commercially as "formalin," contains about 40 per cent of formaldehyde. For analysis, dilute 10 ml of the formaldehyde solution to 400 ml, and of this 1 per cent solution, take 5 ml (= 0.125 ml of the original solution) for analysis. Add 40 ml of 0.1 N iodine solution, and immediately afterwards strong sodium hydroxide solution, drop by drop, until the color of the solution is a light yellow; allow to stand for 10 minutes. Then make the solution acid with hydrochloric acid, and titrate the excess iodine with 0.1 N sodium thiosulfate solution.

* The HI acts as a catalyzer according to Volhard.

† *Z. angew. Chem.*, **1904**, 580.

‡ *Z. anal. Chem.*, **36**, 19 (1897).

36. Determination of Ferricyanic Acid*

$$1 \text{ l of } 0.1\,N \text{ iodine solution} = \frac{K_3Fe(CN)_6}{10} = 32.92 \text{ g}$$

Principle. — If a neutral solution of potassium ferricyanide is treated with an excess of potassium iodide, the ferricyanide ion is reduced to ferrocyanide ion with separation of free iodine:

$$2\,K_3Fe(CN)_6 + 2\,KI \rightleftarrows 2\,K_4Fe(CN)_6 + I_2$$

Lenssen titrated the liberated iodine with sodium thiosulfate, but the results are not concordant, because the reaction is a reversible one. The reaction is quantitative, however, as Mohr first showed, if the ferrocyanide is removed from the solution as fast as it is formed. This is accomplished, according to Mohr, by adding an excess of zinc sulfate, free from iron, to the solution. According to the experiments of E. Müller and O. Diefenthäler,† the titration should take place in a solution which is as nearly neutral as possible, but not in one made alkaline by the addition of sodium bicarbonate (see p. 638).

Müller and Diefenthäler's Procedure. — Weigh out 0.7 g of the ferricyanide into a glass-stoppered flask, dissolve in about 50 ml of water, and treat with 3 g of potassium iodide and 1.5 g of zinc sulfate free from iron. If an acid solution of ferricyanide is to be analyzed, carefully neutralize with caustic soda until barely alkaline and then made acid with a drop of sulfuric acid. Alkaline solutions must always be neutralized with acid.

37. Determination of Ferri- and Ferrocyanide in the Presence of One Another

In one sample determine ferricyanide iodometrically as just described and in another sample determine ferrocyanide by permanganate titration (p. 573).

38. Determination of Phenol. Method of W. Koppeschaar‡

$$1 \text{ l of } 0.1\,N\ Na_2S_2O_3 = \frac{C_6H_5OH}{60} = 1.568 \text{ g } C_6H_5OH$$

Principle. — If an aqueous solution of phenol is treated with an excess of bromine, the phenol is converted quantitatively into tribromophenol:

$$C_6H_5OH + 3\,Br_2 = 3\,HBr + C_6H_2Br_3(OH)$$

The tribromophenol is a pale yellow, crystalline substance which is quite insoluble in water (43.7 l of water dissolve 1 g of tribromophenol). If, after the reaction

* Lenssen, *Ann. Chem.*, **91**, 240. Mohr., *ibid.*, **105**, 60.
† *Z. anorg. Chem.*, **1910**, 418.
‡ *Z. anal. Chem.*, **15**, 233 (1876).

has taken place, potassium iodide is added to the solution, iodine is liberated corresponding to the excess of bromine, and by titrating this iodine with sodium thiosulfate solution, it is easy to find how much bromine reacted with the phenol.

Requirements. — 0.1 N bromine solution and 0.1 N sodium thiosulfate solution. On account of the volatility of free bromine, Koppeschaar uses a solution of potassium bromate and bromide which, upon being acidified, gives a known amount of bromine in accordance with the equation:

$$KBrO_3 + 5\,KBr + 6\,HCl = 6\,KCl + 3\,H_2O + 3\,Br_2$$

Thus, to obtain 0.1 N bromine solution which will keep indefinitely, dissolve *exactly* 2.784 g of pure potassium bromate (dried at 100°) and about 10 g of potassium bromide in water and dilute the solution to 1 l at 20°. An excess of bromide does no harm.

Procedure. — Weigh out 5 g of phenol in a weighing-beaker, dissolve in a little water, rinse the solution into a liter flask, and shake well. Of this solution, pipet off 100 ml, transfer to another liter flask, dilute with water to the mark, mix and transfer 100 ml of this solution to a stoppered bottle of about 250-ml capacity, treat with 50 ml of the bromate solution, shake, make acid with 5 ml of concentrated hydrochloric acid, shake again, and allow to stand 15 minutes. Then add 2 g of potassium iodide and titrate the liberated iodine, corresponding to the excess of bromine, with 0.1 N thiosulfate solution, using starch as indicator. Then if t milliliters of the last solution are used and the weight of phenol was a grams:

$$\frac{(50 - t) \times 0.1568}{a} = \text{per cent phenol}$$

Remark. — Before making an analysis, a blank experiment should always be made with the bromate solution to make sure that its strength corresponds to the theoretical value.

This method is suitable for the analysis of pure preparations of phenol (carbolic acid) but not for crude phenol, creosote oil, etc.

39. Determination of Thiocyanate. Method of Treadwell-Mayr

$$1\text{ l of }0.1\,N\ KBrO_3\text{ solution} = \frac{HCNS}{60} = 0.9847\text{ g }HCNS$$

In acid and neutral solution thiocyanate does not react with iodine but in alkaline solution the following reaction takes place:

$$KCNS + 4\,H_2O + 4\,I_2 = KHSO_4 + 7\,HI + CNI$$

The reaction takes place very slowly. The oxidation is effected much more rapidly with a bromate-bromide solution.

Procedure. — Treat a measured volume of thiocyanate solution with a measured volume of 0.1 N potassium bromate solution and 2–3 g of potassium bromide in the liter bottle shown in Fig. 120, p. 630.

Evacuate with suction and close the stopcock. Introduce 30–40 ml of 6 N hydrochloric acid for each 100 ml of solution without letting in any air. Shake well. After standing 10 minutes, rinse out the funnel with water and add 2–3 g of potassium iodide dissolved in a little water. Shake and then titrate the liberated iodine with 0.1 N thiosulfate.

If T is the volume of 0.1 N bromate solution and t the volume of 0.1 N thiosulfate, then

$$(T - t)\frac{\text{HCNS} \times 100}{60{,}000 \times a} = \frac{(T - t)\ 0.09847}{a} \text{ per cent HCNS}$$

D. Ceric Sulfate Method

Cerium forms colorless cerous salts in which it has a valence of 3 and yellow or orange ceric salts in which it has a valence of 4. Cerous salts can be oxidized to ceric salts in acid solutions (*a*) by heating with lead dioxide and 5 N nitric acid, (*b*) by heating with ammonium persulfate, (*c*) by electrolysis, and (*d*) by sodium bismuthate.

$$2\,Ce^{+++} + PbO_2 + 4\,H^+ = 2\,Ce^{++++} + Pb^{++} + 2\,H_2O$$
$$2\,Ce^{+++} + S_2O_8^{--} = 2\,Ce^{++++} + 2\,SO_4^{--}$$
$$2\,Ce^{+++} + NaBiO_3 + 6\,H^+ = 2\,Ce^{++++} + Na^+ + Bi^{+++} + 3\,H_2O$$

As a result of the oxidation, the colorless cerous solution becomes yellow or orange. If a solution of a cerous salt is treated with an excess of alkali hydroxide and chlorine gas is led through the solution, the white cerous hydroxide, $Ce(OH)_3$, which forms when the solution is made basic, is changed to light yellow ceric hydroxide, $Ce(OH)_4$. The precipitate of ceric hydroxide dissolves in nitric acid yielding a red solution, but when acted upon by hydrochloric acid, colorless cerous chloride is formed and chlorine is evolved as a result of the oxidation of some of the hydrogen chloride.

The normal potential corresponding to the reaction $Ce^{+++} = Ce^{++++} + \epsilon$ is -1.45 volts. If we compare this with the reaction $Mn^{++} + 4\,H_2O = MnO_4^- + 8\,H^+ + 5\,\epsilon$ which has a normal potential of -1.52 volts and with the reaction $2\,Cr^{+++} + 7\,H_2O = Cr_2O_7^{--} + 6\,\epsilon$ which has a normal potential of -1.3 volts, we see that ceric sulfate is a stronger oxidizing agent than potassium dichromate and is nearly as strong as potassium permanganate. Ceric sulfate solutions are less sensitive to hydrochloric acid than are solutions of potassium permanganate, and there is but one possible reduction product. Were it not for the fact that ceric salts are much more expensive than equivalent quantities of permanganate, doubtless the use of these salts as oxidation agents would be far more prevalent. On the other hand, the cost of the reagent is by no means prohibitive, and it is already being used widely. Like permanganate and unlike potassium dichromate, the ceric salt is not suitable for use as a primary standard or, in other words, a standard solution cannot be obtained by weighing out an exact quantity of the reagent. The reagent should be prepared by dissolving approximately the proper quantity of ceric salt, and the solution should then be standardized by titration against sodium oxalate or a solution containing ferrous salt.

Ceric solutions, like those of potassium permanganate, can serve as their own indicators for the titration of colorless solutions, but the color change is not so marked

and it requires a little more of the ceric solution to impart a perceptible tint to the fully titrated solution. In the titration of ferrous salts with ceric sulfate it is best to add phosphoric acid to form the colorless ferric acid phosphate complex and to use diphenylamine sulfonic acid as indicator. Diphenylamine itself, diphenylbenzidine, and some similar organic compounds can also be used as indicators. These indicators form oxidation products which have colors easily distinguishable from the colors of the unoxidized compounds, and the oxidation-reduction potential is such that the organic compound is not oxidized until after practically all the substance being titrated has entered into the reaction; in other words, the color change takes place when the desired oxidation of the substance being analyzed has been completed.

Preparation of 0.1 *N* Ceric Sulfate Solution.* — Ceric sulfate solutions can be prepared by digesting the oxide, CeO_2, with strong sulfuric acid at 125° or higher, cooling, and diluting. The solution after being diluted should be 1–2 *N* in sulfuric acid. Ceric oxide of suitable purity can be purchased as such, or it may be made by igniting cerous oxalate, which is one of the cheapest cerium salts, to 600–625° for about 10 hours.

It is far more convenient to use pure ceric ammonium sulfate, $Ce(SO_4)_2 \cdot 2\,(NH_4)_2SO_4 \cdot 2H_2O$, which can now be purchased from dealers in chemicals and has the high molecular weight of 632.5. Weigh out approximately 65 g of the salt, add 500 ml of 2 *N* sulfuric acid, and stir till all the solid has dissolved. Dilute to about 1 l, mix well, and keep in a glass-stoppered bottle.

Standardization. (*a*) *Against Sodium Oxalate.* — Weigh out carefully into 400-ml beakers duplicate portions of 0.25–0.30 g of pure sodium oxalate and dissolve each sample in 200–250 ml of boiling-hot water. To each solution add 10 ml of 18 *N* sulfuric acid and titrate with the ceric sulfate solution until 1 drop of the reagent changes the solution from colorless to light yellow. Run a blank analysis in the same way with the same quantities of acid and water, but without any sodium oxalate, to determine how much of the ceric sulfate solution is required to impart a perceptible color to the volume of liquid used. Deduct this volume (usually about 0.05 ml) from the volumes used in the titrations against sodium oxalate. Compute the normality of the ceric solution in exactly the same way as in the standardization of potassium permanganate (p. 547).

$$C_2O_4^{--} + 2\,Ce^{++++} \rightarrow 2\,Ce^{+++} + 2\,CO_2$$

(*b*) *Against Pure Iron.* — Weigh out accurately portions of 0.025–0.030 g into 400-ml beakers; add 5 ml of water and 10 ml of concentrated hydrochloric acid. Heat gently until all the metal has dissolved.

* Willard and Young, *J. Am. Chem. Soc.*, **50**, 1322, 1334, 1372 (1928). Willard and Furman, *Elementary Quantitative Analysis*.

Unless particular precautions are taken to avoid oxidation (see p. 548) the solution will show a slight yellow color, due to the formation of a little ferric chloride as a result of atmospheric oxidation; hydrochloric acid alone can only oxidize iron to the ferrous state. To convert all the iron to the ferrous condition, carefully add stannous chloride solution (see p. 555) until the hot solution no longer shows any yellow color, but avoid adding an excess of the reagent. Cool, by placing the beaker in running water, dilute to 150 ml, and add 10 ml of mercuric chloride solution (cf. p. 555). A white, silky precipitate of mercurous chloride should be formed. If the precipitate is dark in color or is bulky, it is best to throw the solution away and start again. To the ferrous solution add 10 ml of phosphoric acid, *d.* 1.37, and 0.3 ml of 0.01 *M* diphenylamine sodium sulfonate. (To prepare this indicator solution, dissolve 0.32 g of the barium salt in 100 ml of water, add 0.5 g of solid sodium sulfate, stir well, and allow the barium sulfate precipitate to settle. Decant off the clear solution.) Titrate with the ceric sulfate solution until the solution assumes a distinct purple tint. The reaction between the indicator and the ceric sulfate is rapid but not instantaneous; the reagent should be added slowly toward the last.

$$Fe^{++} + Ce^{++++} \rightarrow Fe^{+++} + Ce^{+++}$$

Determination of Iron in an Iron Ore

Dissolve 0.25–0.30 g of the powdered ore by heating gently with 20 ml of 6 *N* hydrochloric acid exactly as described on p. 555. After the reduction with stannous chloride and treatment with mercuric chloride, add 10 ml of phosphoric acid, *d.* 1.37, and 0.3 ml of 0.01 *M* diphenylamine sodium sulfonate indicator solution. Titrate with ceric sulfate solution as just described for the standardization of the solution against pure iron.

Ceric sulfate can be used for many other oxidations. It oxidizes hydrogen peroxide, nitrous acid, hydrazine, hydroxylamine, hydrazoic acid, tartaric acid, oxalic acid, anthracene, sodium thiosulfate, sulfurous acid, and hypophosphorous acid as well as many other substances. Some of these reactions can be utilized for various titrations. Thus the oxidation of the oxalate ion can be used not alone for standardizing the ceric solution but also for determining cations like calcium, strontium, lead, etc., which form insoluble oxalates. The filtered precipitates all yield oxalic acid, when digested with dilute acid, and the oxalic acid can be titrated with ceric sulfate.

Reduction Methods

1. Determination of Ferric Iron (Fresenius)*

In all methods thus far discussed, it was necessary to reduce the iron to the ferrous condition before it could be determined volumetrically. In the following method, first suggested by Penny and Wallace,† but improved by Fresenius, the iron in the *ferric* condition may be determined with accuracy and rapidity.

The hydrochloric acid solution containing ferric chloride is titrated hot with stannous chloride solution until the former becomes colorless. By this means the ferric salt is reduced to ferrous salt:

$$2\ FeCl_3 + SnCl_2 = SnCl_4 + 2\ FeCl_2$$

Inasmuch as it is not very easy to determine the end point with accuracy, because the last part of the iron is reduced very slowly, it is customary to run over the end point and to titrate the excess of the stannous chloride with iodine solution.

Solutions Required. 1. *A Ferric Chloride Solution Containing a Known Amount of Iron.* — Dissolve exactly 10.03 g of pure iron wire in 150 ml of 6 *N* hydrochloric acid in a long-necked flask held in an inclined position; oxidize the iron with potassium chlorate, and boil off the excess of chlorine. Transfer the ferric chloride solution to a liter flask and dilute to the mark with water; 50 ml of this solution contain 0.5 g of pure iron.‡

2. *A Stannous Chloride Solution.* — Heat 25 g of tinfoil in a covered porcelain dish for 2 hours on the water-bath with 50 ml of 8 *N* hydrochloric acid and a few drops of chloroplatinic acid to form a Pt-Sn couple which helps dissolve the tin. Add 150 ml more of hydrochloric acid and an equal volume of water, filter, and dilute to 1 l. As stannous chloride is oxidized by contact with the air, keep the solution in a flask which on one side is connected with the buret as shown in Fig. 109, p. 501, and on the other side with a Kipp carbon dioxide generator.

3. *An Iodine Solution, Approximately Tenth-normal.*

Procedure. — (*a*) Standardization of the Solutions.

First titrate the stannous chloride and iodine solutions against each other. Measure out 2 ml of the former with a pipet, dilute to about 60 ml, add a little starch solution, and titrate the mixture with iodine until a blue color is obtained.

Next, titrate 50 ml of the acid ferric chloride solution against the stannous chloride solution.

(*b*) *Determination of Iron in Hematite.* Roast 5 g of the finely divided ore at a dull red heat to destroy any organic matter which may be present,

* *Z. anal. Chem.*, **1**, 26.

† *Dingl. polyt. J.*, **149**, 440.

‡ The assumption being made that the iron wire contained 99.7 per cent pure iron.

place the powder in a long-necked flask, and heat with 25 ml of concentrated hydrochloric acid and a little potassium chlorate until all the iron oxide is dissolved, leaving a white sandy residue. Add 20 ml more of hydrochloric acid and continue the boiling, while passing a current of air through the solution, until all the excess of chlorine is completely removed and the escaping vapors will no longer set free iodine when passed into a potassium iodide solution. Dilute the solution thus obtained to exactly 500 ml and use 50 ml for the analysis.

Example

1. *Standardization of the reagents:*

2 ml of stannous chloride solution require 7.2 ml of iodine solution. 1 ml iodine solution	= 0.278 ml $SnCl_2$
50 ml ferric chloride solution (= 0.5 g iron) require for decolorization	30.34 ml $SnCl_2$
and for the titration of the excess 0.51 ml of iodine solution = 0.51 × 0.28	0.14 ml $SnCl_2$
Consequently, 50 ml ferric chloride solution = 0.5 g iron	= 30.20 ml $SnCl_2$

and 1 ml $SnCl_2 = \frac{0.5}{30.20} = 0.01656$ g Fe.

2. *Titration of the solution to be analyzed:*

50 ml (= 0.5 g of iron ore) require	18.96 ml $SnCl_2$
and for the titration of the excess, 0.64 ml of iodine = 0.64 × 0.28	= 0.18 ml $SnCl_2$
so that 0.5 g of ore corresponds to	18.78 ml $SnCl_2$
and contain, therefore, 18.78 × 0.01656 = 0.3110 g Fe	= 62.20% Fe

2. Determination of Tin by Ferric Chloride*

This method is suitable for determining tin in tin-plating baths.

Principle. — When a ferric chloride solution is added to a solution containing stannous chloride it is decolorized, then a pale greenish ferrous solution is obtained, and finally, when an excess of ferric chloride is present, a yellowish tint is easily recognized as the end point. If, when the titration is made in this way, so much pale green ferrous salt is formed that the end point is hard to recognize, this difficulty can be overcome by first oxidizing the greater part of the tin with normal potassium chlorate solution.

$$SnCl_2 + 2\ FeCl_3 = SnCl_4 + 2\ FeCl_2$$
$$3\ SnCl_2 + KClO_3 + 6\ HCl = 3\ H_2O + KCl + 3\ SnCl_4$$

Requirements. — 1. Normal potassium chlorate solution. Dissolve 20.43 g of pure potassium chlorate, dried at 120°, in a little water and dilute with water at 20° to 1 l.

2. Normal ferric chloride solution. Dissolve 56 g of pure iron in 600 ml of 6 N hydrochloric acid. Heat toward the last, and gradually introduce 20 g of potassium chlorate. Boil till all the excess chlorine is removed, dilute to about 900 ml, filter if necessary, and dilute to exactly 1 l at 20°.

* Method of O. Meister.

Standardization of the Ferric Chloride Solution and Simultaneous Determination of the Tin Content of a Solution. — Transfer 25 ml of the tin solution, which should contain about 30 g of tin in 300 ml of 6 N hydrochloric acid, into a 200-ml flask held in an inclined position. Add 0.3 g of aluminum powder, which will cause the precipitation of metallic tin. After the evolution of hydrogen ceases, add 20 ml of concentrated hydrochloric acid, place a small funnel in the neck of the flask, and heat till all the tin is dissolved again. Rinse out the funnel and the neck of the flask with hot water and run in ferric chloride solution from a buret into the boiling solution until the greenish yellow end point is obtained. Call the volume of ferric chloride solution T.

Reduce another portion of the tin solution in exactly the same way but instead of adding ferric chloride solution, first oxidize the greater part of the tin with t milliliters of N potassium chlorate solution and finish with t_1 milliliters of the ferric chloride solution. Evidently $T - t_1$ milliliters of the ferric chloride solution are equivalent to t milliliters of N potassium chlorate and 1 ml of $FeCl_3$ solution $= \dfrac{t}{T - t_1} =$ f milliliters of N solution $= f \times 0.05935$ g of Sn. The tin content of the original solution is then

$$\frac{T \times f \times 59.35}{25} \text{ g Sn per liter}$$

3. Determination of Ferric Iron by Means of Titanous Chloride (Knecht and Hibbert)*

$$1000 \text{ ml of } 0.1\,N\ TiCl_3 \text{ solution} = \frac{Fe}{10} = 5.585 \text{ g Fe}$$

Principle. — If an acid solution of a ferric salt is treated with titanous chloride, the iron is immediately reduced in the cold to the ferrous condition:

$$FeCl_3 + TiCl_3 = TiCl_4 + FeCl_2$$

Preparation of Titanous Chloride Solution. — A concentrated solution of titanous chloride, prepared by the electrolysis of $TiCl_4$, can now be obtained on the market. To such a solution add an equal volume of concentrated hydrochloric acid, boil to expel any hydrogen sulfide, and dilute with ten times as much boiled water.

Preserve the solution in contact with an atmosphere of hydrogen, or carbon dioxide, in a bottle such as is shown in Fig. 109, p. 501, which is connected with a buret, and in this case with a Kipp hydrogen, or carbon dioxide, generator instead of the soda-lime tube.

* *Ber.*, **36**, 1551 (1903). $TiCl_3$ is a very efficient reducing agent and has been used for many determinations. Cf. Knecht and Hibbert, *New Reduction Methods in Volumetric Analysis*, Longmans, Green & Co.

Standardization of the Titanous Chloride Solution. — Prepare a ferric chloride solution of known strength as described on p. 645, and of this solution measure out 50 ml into a beaker, and slowly add the titanium trichloride with constant stirring, while a current of carbon dioxide is constantly being passed into the beaker. After the solution is nearly decolorized, introduce a drop of potassium thiocyanate solution, and continue the adding of titanous chloride to the disappearance of the red color.

The analysis proper is carried out in exactly the same manner.

4. Determination of Ferrous and Ferric Iron by the Titanium Method

First titrate the ferrous iron with permanganate in the presence of manganous sulfate (cf. p. 552), and then determine the total iron with titanous chloride.

The method can be carried out very rapidly, and the results are accurate.

5. Determination of Titanium

Reduce the quadrivalent titanium to the trivalent condition and titrate with methylene blue solution.*

6. Determination of Hydrogen Peroxide*

If titanous chloride is run into an acid solution of hydrogen peroxide, the latter is colored first yellow, then a deep orange, and as soon as the maximum depth of color is produced, it begins to fade upon the further addition of titanous chloride until finally the solution becomes colorless, which is taken as the end point.

The reaction takes place in two stages:

$$2\,TiCl_3 + 3\,H_2O_2 + 2\,H_2O = 2\,H_2TiO_4 + 6\,HCl$$
$$H_2TiO_4 + 2\,TiCl_3 + 6\,HCl = 3\,TiCl_4 + 4\,H_2O$$

or combining the two equations:

$$2\,TiCl_3 + H_2O_2 + 2\,HCl = 2\,TiCl_4 + 2\,H_2O$$

On account of the fact that the reducing value of the titanous chloride solution is not very permanent, it should be standardized against ferric chloride before each series of experiments.

If t milliliters of titanous chloride solution of which 1 ml = α grams Fe were required for the reduction of 1 ml of hydrogen peroxide, then

$$\frac{34.02 \times \alpha t}{111.7} \text{ grams } H_2O_2 \text{ are present} = 30.46\,\alpha t \text{ per cent } H_2O_2$$

* Neumann and Murphy, *Z. angew. Chem.*, **1913**, 613.

If it is desired to express the percentage in percentage by volume of active oxygen (cf. p. 571) the following equation holds:

$$10020 \cdot at = \text{per cent oxygen by volume}$$

According to Knecht and Hibbert,* persulfuric acid may likewise be estimated by titration with titanous chloride. The solution of the persulfate is treated with titanous chloride solution and the excess of the latter is titrated with ferric chloride in an atmosphere of carbon dioxide.

7. Determination of Hypochlorous Acid by Means of Arsenious Acid

1 l of 0.1 N Na_2HAsO_3 solution = 3.546 g chlorine

(a) *Method of Penot*†

On adding an arsenite to a solution of a hypochlorite, the former is oxidized to arsenic acid, while the latter is reduced to chloride:

$$^{-} + ClO^{-} = HAsO_4^{--} + Cl^{-}$$

The end point is reached when a drop of the solution added to a piece of iodo-starch paper will cause no blue coloration.

Alkali hypochlorites and chloride of lime may be analyzed by this method and the results obtained are more reliable than those obtained by the iodometric method described on p. 615, for the presence of chlorate has no effect in this case.

(b) *Method of Pontius*

1 l of 0.1 N KI solution = 2.767 g KI = 3.546 g of chlorine

This method is useful for the determination of the available chlorine in bleaching powder and depends upon the fact that potassium iodide is immediately oxidized to iodate by contact with bleaching powder in the presence of sodium bicarbonate solution.

$$3\,\mathbf{CaOCl_2} + KI = KIO_3 + 3\,CaCl_2$$

If potassium iodide solution is added to sodium bicarbonate solution containing bleaching powder and starch paste, a permanent blue color will not be obtained until all the bleaching powder has been decomposed. Then free iodine is formed and the end point is reached.

$$IO_3^- + 5\,I^- + 6\,Ca^{++} + 6\,HCO_3^- \rightarrow 6\,\mathbf{CaCO_3} + 3\,H_2O + 3\,I_2$$

* Knecht and Hibbert, *Ber.*, **38**, 3324 (1905).

† *J. prakt. Chem.*, **54**, 59 (1851).

From these equations it is clear that in this procedure the normal solution of potassium iodide contains only $\frac{1}{6}$ mole of the salt instead of 1 mole.

Procedure. — Triturate 7.092 g of chloride of lime in a porcelain mortar with a little water, rinse into a liter measuring-flask, and fill to the mark with water. Mix thoroughly and without allowing any of the precipitate to settle, transfer with a pipet 50 ml of the liquid to a beaker, add 3 g of sodium bicarbonate, and titrate with potassium iodide until a permanent blue is obtained with starch paste as indicator. In this case the volume of iodide used is the same as the percentage of available chlorine in the sample.

Remark. — Pontius recommends standardizing the potassium iodide solution as follows: Titrate 50 ml of the chloride of lime suspension as above and another portion with 0.1 N arsenite solution by the preceding method of Penot.

III. PRECIPITATION ANALYSES

1. Determination of Silver. Method of Gay-Lussac

This exceedingly accurate determination, which is extensively used for testing silver alloys, depends upon the precipitation of silver chloride from nitric acid solution. Common salt is used as the precipitant.

Solutions Required. 1. *Sodium Chloride Solution of Known Concentration.* — For convenience, it is customary to make the solution of such a strength that 1000 ml correspond to exactly 5 g of silver. To help in getting the end point, however, 0.1 per cent less than the theoretical quantity is used. Weigh out 2.710 g of chemically pure salt, dissolve in distilled water, and dilute to 1 l at 20°.

2. *Decimal Solution of Sodium Chloride.* — Dilute 100 ml of the above solution with distilled water to 1 l.

In laboratories where silver determinations are frequently made, the above solutions are made up in much larger quantities and kept in bottles similar to the one shown in Fig. 109, p. 501. For the stronger solution use a 100-ml pipet and connect the decimal solution with a buret.

Standardization of the Sodium Chloride Solution. — Weigh out exactly 0.5 g of chemically pure silver into a 200-ml flask provided with a well-ground glass stopper, and dissolve in 10 ml of 6 N nitric acid, free from chlorine. Hasten the dissolving by heating on a sand-bath. When the silver has dissolved, heat the solution to boiling to expel the nitrous acid formed. Remove the brown vapors by blowing air into the flask. As soon as no more of these are formed, remove the flask from the sand-bath and allow to cool. To the silver solution add exactly 100 ml of the stronger salt solution, stopper the flask, and

vigorously shake until the precipitated silver chloride collects together, and the supernatant liquid appears clear.

As the salt solution was made up a little weak, the precipitation of the silver is not quite complete and consequently more sodium chloride must be added. For this purpose add half a milliliter of the decimal salt solution from the buret, so that the solution runs down the sides of the flask upon the surface of the liquid, causing a distinct cloud of silver chloride to be formed. Shake the liquid, allow the precipitate to settle, again treat with half a milliliter of the decimal salt solution, and repeat the process until finally the addition of the salt solution fails to produce any further turbidity; the last half cubic centimeter is not used in the calculation.

Example. — 0.5 g of chemically pure silver ($\frac{1000}{1000}$ fine) required 100 ml of the standard salt solution + 1 ml of the decimal solution, *i.e.*, 100.1 ml of the salt solution correspond to 1000 silver;* this is the value of the salt solution.

Silver Determination. — To obtain absolutely accurate results it is necessary to employ the same amount of silver for the analysis as was used in the standardization of the solution; consequently the approximate amount of silver present in the alloy must be determined. This can be accomplished by cupellation, or volumetrically by the method of Volhard, described further on.

Example. — It was found by cupellation that an alloy contained about $\frac{800}{1000}$ fine silver; for the titration an amount must be taken which will contain 0.5 g of silver; we have then, $1 : 0.8 = x : 0.5$, $x = 0.625$ g.

Weigh out, therefore, 0.625 g (= 1250†) of the alloy and proceed exactly as in the standardization.

For the precipitation of the silver, 1250 parts of alloy require 100 ml of the standard salt solution + 3 ml of the decimal solution, *i.e.*, 1250 parts of the alloy require 100.3 ml of the standard salt solution. Since 100.1 ml of this salt solution correspond to 1000 parts of pure silver, there must be $\frac{1000 \times 100.3}{100.1}$ alloy;

so that in 1000 parts of the alloy there will be $\frac{1002 \times 1000}{1250}$ 801.6 parts of silver.

This procedure is designated as the French method in contrast to the German or Dutch method. In the latter case, 0.5 g of the alloy (= 100) is weighed out and the same amount of silver is added which

* For convenience in calculation, 0.5 g of pure silver is designated by 1000, 0.25 g by 500, and 0.1 g by 250, etc.

† If 0.5 g = 1000, then $0.5 : 1000 = 0.625 : x$; $x = 1250$.

the alloy lacks in fineness. In this way one more weighing is necessary, but the calculation is somewhat simpler.

Example. — By cupellation an alloy is found to contain $\frac{800}{1000}$ silver. In order to make the silver equal 1000, 200 parts of fine silver must be added. For the analysis, therefore, 0.5 g of the alloy and 0.1 g of pure silver (= 200) are taken, dissolved in nitric acid, and titrated with sodium chloride.

2. Determination of Silver. Method of Volhard

$$1 \text{ l of } 0.1\,N \text{ KCNS} = \frac{\text{Ag}}{10} = 10.79 \text{ g Ag}$$

If to a silver solution containing ferric-ammonium alum, free from chloride but containing enough nitric acid to discharge the brown color of the iron salt, a solution of alkali thiocyanate is added, white insoluble silver thiocyanate is precipitated:

$$AgNO_3 + KCNS = KNO_3 + \mathbf{AgCNS}$$

When all the silver is precipitated, the next drop of the thiocyanate solution will cause a permanent red coloration due to the formation of ferric thiocyanate.

Requirements. 1. *Tenth-normal Potassium (or Ammonium) Thiocyanate Solution.* — As both these salts are hygroscopic and cannot be dried without decomposition, an exactly tenth-normal solution cannot be prepared by weighing out the solid salt. Dissolve approximately the right amount (about 10 g KCNS or 9 g NH_4CNS) in a liter of water.

Ferric-ammonium Alum Solution. — A cold, saturated solution of ferric alum to which enough nitric acid is added to cause the disappearance of the brown color. Use about 3.5 g of the alum, 10 ml of water, and 2 ml of 6 N HNO_3. Of this indicator use the same amount for all titrations, about 2–3 ml for 100 ml of the silver solution.

Standardization of Thiocyanate Solution

Weigh out portions of about 0.4 g of pure silver nitrate and dissolve in 100 ml of 0.3 N nitric acid. Add 5 ml of indicator solution and titrate with thiocyanate solution to a permanent red tinge in the solution. Or dissolve 0.25-g portions of pure silver in 15 ml of 6 N nitric acid. Dilute to about 25 ml, boil till all nitrous fumes are expelled, add 75 ml of cold water and 5 ml of indicator solution, and titrate with thiocyanate.

Determination of Silver in Silver Alloys

Dissolve 0.5 g of the brightly polished metal in 10 ml of 6 N nitric acid. After the silver has dissolved, dilute with 50 ml of water and

boil to expel nitrous fumes.* Cool, add 2–3 ml of the ferric alum solution, and titrate with the thiocyanate solution as in the standardization. The presence of metals whose salts are colorless does not influence the accuracy of this determination, except that mercury must be absent because its thiocyanates are insoluble. Nickel and cobalt must not be present to any extent, because their salts are colored, and not more than 60 per cent of copper in an alloy is permissible. If more copper is present the following procedure must be used: Precipitate the silver by means of an excess of alkali thiocyanate, wash completely with water, place the funnel over an Erlenmeyer flask, break the apex of the filter, wash its contents into a flask by means of concentrated nitric acid, and heat the liquid to gentle boiling for three-quarters of an hour. As the sulfuric acid formed will have some influence upon the subsequent titration, dilute the solution with water to about 100 ml, and add a concentrated barium nitrate solution, drop by drop, until all the sulfuric acid is precipitated. Then titrate the silver with thiocyanate solution without filtering off the barium sulfate.

3. Determination of Mercury

Mercuric thiocyanate, like silver thiocyanate, is so insoluble that the nitrate or sulfate solution can be titrated with standard thiocyanate solution using ferric alum as indicator. The method fails, however, when chloride is present because mercuric chloride is so slightly ionized that it does not react completely. This constitutes the principal reason why the method is not used in preference to other methods, because hydrochloric acid is commonly used in dissolving the sample and the complete removal of chloride without volatilization of any mercuric chloride is difficult. The titration gives excellent results in a nitrate or sulfate solution and can be carried out in the presence of lead, copper, bismuth, cadmium, tin, arsenic, antimony, thallium, iron, zinc, manganese, nickel, and cobalt. Mercurous salt, silver, and nitrous acid should be absent.

Procedure. — To the solution containing 0.05 to 0.3 g of mercury as sulfate or nitrate in a volume of about 100 ml, add nitric or sulfuric acid sufficient to make the solution about 1.5 N in acid and, to make sure of the absence of nitrous acid or mercurous iron, add 5 per cent permanganate solution dropwise until a red color is produced, or a manganese dioxide precipitate is formed, which persists for 5 minutes. Destroy the excess permanganate, or dissolve the precipitate, by the

* Nitrous acid reacts with thiocyanic acid, forming a red compound which may easily be mistaken for ferric thiocyanate.

addition of a very little ferrous sulfate or some hydrogen peroxide. Titrate as described for the determination of silver but, as the color of ferric thiocyanate is noticeable before the end of the titration and disappears very slowly at the last, make sure that the solution is not under-titrated and that a distinct red color persists after vigorous shaking or stirring.

Prepare the standard solution of thiocyanate and the indicator solution of ferric alum as described under the determination of silver. It is best, however, to standardize the solution of thiocyanate by direct titration against 0.25–0.30 g mercury that has been dissolved in hot $6\,N$ nitric acid and titrated under the conditions outlined above.

4. Determination of Chloride

(a) *Volhard's Method*

$$1 \text{ l of } 0.1\,N\ AgNO_3 \text{ solution} = \frac{Cl}{10} = 3.546 \text{ g chlorine}$$

According to Volhard's original directions, the chloride solution was treated with $0.1\,N$ silver nitrate solution and then, without filtering off the precipitate, 5 ml of the ferric-ammonium alum solution were added and the excess of silver titrated with $0.1\,N$ potassium or ammonium thiocyanate (see p. 653).

The results are satisfactory with large quantities of chloride, but in the titration of small quantities of chloride too high results are obtained, as was first shown by G. Drechsel* and later confirmed by M. A. Rosanoff and A. E. Hill.† Drechsel showed that it was impossible to get the true end point of the reaction, as the red coloration gradually disappeared on stirring, remaining permanent only after a considerable excess of thiocyanate had been added. The reason for this is that silver chloride is more soluble than silver thiocyanate. Thus the precipitate gradually reacts with the red ferric thiocyanate, as follows:

$$3\,\mathbf{AgCl} + Fe(CNS)_3 = 3\,\mathbf{AgCNS} + FeCl_3$$

To avoid this error Drechsel proceeds as follows:

To the chloride solution in a 200-ml measuring-flask, add an excess of $0.1\,N\ AgNO_3$ solution, make the solution acid with nitric acid, and shake the stoppered flask until the precipitate coagulates enough to give a clear supernatant liquid. Dilute the solution to the mark, thoroughly mix, and filter through a dry filter, rejecting the first 10 ml of filtrate. Of the filtrate, take 50 or 100 ml, add the ferric alum indicator, and titrate the excess of silver with $0.1\,N$ thiocyanate solution. The results thus obtained are excellent.

* *Z. anal. Chem.*, **16**, 351 (1877).

† *J. Am. Chem. Soc.*, **29**, 269.

Remark. — V. Rothmund and A. Burgstaller* found that it is possible to obtain correct results without filtering off the silver chloride precipitate. They heated the solution after the addition of the excess of silver nitrate, until the precipitate coagulated thoroughly, in which form it reacted less readily with a soluble thiocyanate. After cooling, the ferric alum indicator was added and the titration finished. Rothmund and Burgstaller also found that the coagulation of the silver chloride precipitate by ether† sufficed to make the filtration unnecessary. The chloride solution is placed in a flask with tightly fitting glass stopper, 5 ml of ether added, and an excess of silver nitrate solution. After shaking a few minutes, the supernatant solution becomes clear and the titration can be finished with accuracy.

Adsorption Indicators. — Fajans and his collaborators‡ have shown that silver halide precipitates, owing to their colloidal properties, tend to adsorb excess Ag^+ or excess halogen ions from the solution with which they are in contact. The adsorbed Ag^+ has the property of dragging down with it the anions of certain organic dyestuffs, which are of a feebly acidic nature, and a change of color takes place as a result of the adsorption. Thus fluorescein in aqueous solution has a rose color. When silver chloride is formed in the presence of a very slight excess of Ag^+, the anion of fluorescein is adsorbed and there is a change of color to reddish violet. If a very little of the indicator is present, the silver chloride precipitate assumes a reddish tint as soon as there is a very slight excess of Ag^+ present.

In the titration of Cl^- with Ag good results are thus obtained in neutral solutions with fluorescein as indicator. To prepare the indicator solution, dissolve 0.2 g of the sodium salt of fluorescein in 100 ml of water or dissolve 0.2 g of fluorescein itself in 100 ml of alcohol. Use about 2 drops of indicator solution for each 10 ml of 0.1 *N* chloride solution to be titrated with 0.1 *N* silver nitrate solution. The results are accurate, even in the presence of considerable quantities of alkali cations, provided the chloride solution is at least 0.005 *N* in halogen ions. Alkaline-earth cations interfere somewhat.

Bromides, iodides, and thiocyanates can be titrated in dilute solutions, even in the presence of dilute nitric acid, when eosin is chosen as the indicator. Two drops of the 0.5 per cent aqueous solution should be used for each 10 ml of 0.1 *N* halide to be titrated. The silver halide precipitate becomes red colored at the end point. Eosin cannot be used for the titration of chlorides with silver nitrate because the eosin is adsorbed and colors the silver chloride precipitate before the end point is reached. Fluorescein, on the other hand, can be used with chlorides, bromides, iodides, or thiocyanates.

In the titration of silver solutions, there are two ways in which an adsorption indicator can be used. An excess of standard halide solution can be added and the excess titrated with standard silver nitrate solution using fluorescein or eosin as indicator or a slightly basic indicator can be used such as "rhodamine 6 G." In this case the cations of the indicator are adsorbed by the precipitate as soon as a slight excess of Br^- has been added and a color change takes place with the precipitate assuming a bluish violet hue. Nitric acid can be present during this titration with the basic indicator provided the concentration is not over 0.5 *N* in acid.

A number of other organic dyestuffs can be used as adsorption indicators. Thus

* *Z. anorg. Chem.*, **63**, 333 (1909).

† Cf. E. Alefeld, *Z. anal. Chem.*, **48**, 79 (1909).

‡ *Z. physik. Chem.*, **97**, 478 (1921); **105**, 255 (1923); *Z. Electrochem.*, **29**, 495 (1923); *Naturwiss*, **11**, 165 (1923); *Z. anorg. allgem. Chem.*, **137**, 221 (1924).

Kolthoff* reports good results with "tropeolin yellow 00," "bromophenol blue," and "metanil yellow" in titrating dilute chloride solution with 0.1 N silver nitrate.

(b) *Fr. Mohr's Method*

If the neutral solution of an alkali or alkali-earth chloride containing a few drops of potassium chromate solution is treated with silver nitrate solution, added from a buret, a red precipitate of silver chromate is formed which, on stirring, disappears on account of its being decomposed by the alkali chloride to silver chloride and alkali chromate:

$$\mathbf{Ag_2CrO_4} + 2\,NaCl = 2\,\mathbf{AgCl} + Na_2CrO_4$$

When all the chlorine is changed to insoluble silver chloride, the next drop of the silver solution will impart a permanent reddish color to the liquid. For small amounts of chloride in concentrated solutions this method gives very sharp results. If, however, the volume of the solution is too large, the results are not very accurate. A blank experiment must always be made to see how much of the silver solution is necessary to produce the red shade used in the titration when no chloride is present, and this amount must be deducted from that used in the analysis.

Remark. — If it is desired to titrate free hydrochloric acid, first neutralize the solution. With colorless chlorides having an acid reaction ($AlCl_3$), treat the solution with an excess of neutral sodium acetate solution and then titrate. With colored metal chlorides, precipitate the metal with caustic potash or sodium carbonate, filter, wash the precipitate, make the filtrate acid with acetic acid, and then titrate.

5. Determination of Bromide

(a) *Volhard's Method*

$$1\ \text{l of } 0.1\,N\ AgNO_3 \text{ solution} = \frac{Br}{10} = 7.992 \text{ g bromine}$$

Treat the solution of the bromide with an excess of 0.1 N silver solution and titrate with ammonium thiocyanate, using ferric alum as indicator. From the required volume of silver nitrate, compute the quantity of bromine.

Remark. — It is not necessary to filter off the silver bromide, because, unlike the chloride, silver bromide is more insoluble than is silver thiocyanate.

(b) *Fr. Mohr's Method*

The procedure is the same as in the case of the chloride determination.

* *Z. anal. Chem.*, **71**, 235 (1927).

6. Determination of Iodide

Volhard's Method

$$1\ l\ \text{of}\ 0.1\ N\ AgNO_3\ \text{solution} = \frac{I}{10} = 12.69\ g\ \text{iodine}$$

If silver iodide is produced in a solution of an iodide by the addition of silver nitrate, the precipitate will usually enclose a measurable amount of either the soluble iodide or the silver nitrate, so that the analysis cannot be accomplished in the same way as in the analysis of chlorides and bromides.

Place the solution in a glass-stoppered flask, dilute to 200–300 ml, and add the silver solution with vigorous shaking until the yellow precipitate collects together and the supernatant liquid appears colorless. As long as the solution appears milky the precipitation is not complete. Finally add a little more silver nitrate and again shake to precipitate any iodide in the pores of the silver iodide. Then add ferric alum solution, titrate the excess of silver with potassium thiocyanate, and calculate the iodine from the amount of silver used. In this way Volhard obtained exact results.

The ferric solution must not be added before the iodine is completely precipitated, because in acid solution it oxidizes the hydriodic acid with separation of iodine. Silver iodide, however, is without action on ferric salts.

7. Determination of Cyanide. Method of Liebig

$$1\ l\ \text{of}\ 0.1\ N\ AgNO_3\ \text{solution} = \qquad = 13.02\ g\ KCN$$

On adding silver nitrate solution, drop by drop, to a neutral or alkaline solution of an alkali cyanide, a white precipitate is formed when the two liquids first come in contact with one another, but on stirring it redissolves owing to the formation of potassium silver cyanide:

$$\mathbf{AgCN} + KCN = KAg(CN)_2$$

As soon as all the cyanogen is transformed into potassium silver cyanide, the next drop of the silver solution will produce a permanent turbidity:

$$KAg(CN)_2 + AgNO_3 = KNO_3 + 2\,\mathbf{AgCN}$$

The total reaction is, therefore,

$$2\,KCN + AgNO_3 = KNO_3 + KAg(CN)_2$$

1 Ag corresponds to 2 CN, and the end point of the reaction is shown by the formation of a permanent precipitate.

Prepare the alkali cyanide solution in a beaker, add a little potassium hydroxide, and dilute to a volume of about 100 ml. Place the beaker on a piece of black glazed paper and titrate with constant stirring until the turbidity is obtained.

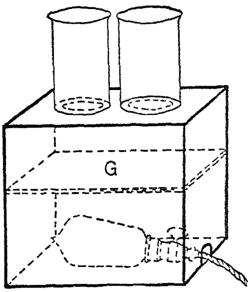

FIG. 123.

For the analysis of free hydrocyanic acid, add an excess of potassium hydroxide solution and treat as above.

The addition of 5 ml of 2 per cent potassium iodide solution slightly increases the sharpness of the end point in the above analysis. The precipitate then consists of silver iodide of which 1 molecule will dissolve in 2 molecules of potassium cyanide, just as silver nitrate does.

Remark. — For the sharp recognition of the end point in this and all other reactions where there is a turbidity, W. D. Treadwell recommends the following arrangement.

The apparatus, Fig. 123, consists of a wooden box in which an incandescent lamp with frosted bowl is placed. Directly over this light are two round holes in the top of the box over which beakers can be placed. Water-bath rings can be used to fit different beakers. The glass plate *G* is used to prevent heating the beakers by the rays from the lamp. To detect a turbidity, place the beaker over the hole, light the lamp, and view horizontally in a dark or dimly lighted room.

8. Determination of Chloride and Cyanide in the Presence of One Another

First, determine the cyanide by the method of Liebig, and then add enough silver solution to convert all the cyanide and chloride into their silver salts. Make the solution acid with nitric acid, dilute with water to a definite volume, filter through a dry filter, and after rejecting the first runnings, use an aliquot part of the filtrate for the titration of the excess of silver by means of potassium thiocyanate, according to Volhard. The calculation of the cyanogen and chlorine is illustrated by the following example:

Ten milliliters of the solution required for the production of a permanent turbidity t milliliters of $0.1\,N$ silver solution. Then an excess of $0.1\,N$ silver solution was added (bringing the total amount used to T milliliters). The solution was acidified with nitric acid, diluted to exactly 200 ml, filtered through a dry filter, and after the usual rejection of the first runnings the excess of the silver was titrated in 100 ml of the filtrate; this required t_1 milliliters of $0.1\,N$ potassium thiocyanate solution. Consequently the amount of cyanogen present is $t \times 0.005202$ g, and the chlorine present amounts to $[T - 2(t + t_1)]\ 0.003546$ g.

9. Determination of Potassium Cyanide in the Presence of Ferrocyanide. Method of W. D. Treadwell*

In this determination the use of potassium iodide is necessary because of the appreciable solubility of silver cyanide in alkali ferrocyanide solution.

Procedure. — To one aliquot part of the solution add 0.1 g of potassium iodide, 2–3 ml of 0.1 N caustic alkali solution or ammonium hydroxide, and titrate in a volume of about 100 ml with 0.1 N silver solution till a turbidity forms. This gives the KCN content.

To determine the ferrocyanide, remove the cyanide by heating another aliquot part of the original solution under a good hood while introducing a stream of carbon dioxide. This requires about 30 minutes. Then titrate the ferrocyanide according to the directions on p. 573.

10. Determination of Thiocyanic Acid. Volhard's Method

$$1 \text{ l of } 0.1\,N\ AgNO_3 \text{ solution} = \frac{HCNS}{10} = 5.907 \text{ g } HCNS$$

This is the reverse of the silver determination (p. 652). Add an excess of 0.1 N silver solution to the solution containing the thiocyanate, and titrate the excess of silver with potassium thiocyanate solution, using ferric alum as indicator.

11. Determination of Thiocyanic and Hydrocyanic Acids in the Presence of One Another

Add enough potassium hydroxide to make the solution neutral, dilute to about 100 ml, and titrate the cyanogen by the method of Liebig (p. 657). Then, add an excess of silver solution, make acid with nitric acid, and titrate the excess of silver with potassium thiocyanate in an aliquot part of the filtrate.

12. Determination of Chloride, Cyanide, and Thiocyanate in the Presence of One Another

In one portion determine the cyanide according to Liebig. To a second portion add an excess of 0.1 N silver solution, make acid with nitric acid, filter, wash the precipitate with water, and titrate the excess of silver in the filtrate according to Volhard. Pierce the filter containing the precipitate and transfer the latter by means of concentrated nitric acid to a flask and boil for three-quarters of an hour. By this

* *Z. anorg. Chem.*, **71**, 219 (1911).

means the cyanide and thiocyanate of silver go into solution, while the silver chloride remains undissolved. Dilute the solution to about 100 ml, add enough barium nitrate to precipitate the sulfuric acid formed, and titrate the silver corresponding to the cyanide and thiocyanate with potassium thiocyanate without filtering off the silver chloride or barium sulfate.

Computation. — If t milliliters of 0.1 N $AgNO_3$ were used in the first titration, then $2\,t$ milliliters would be needed to precipitate all the cyanide. If T milliliters of 0.1 N $AgNO_3$ were required to precipitate all the cyanide, thiocyanate, and chloride, and t_1 milliliters of 0.1 N KCNS were used in the last titration, then

$$t \times 0.005202 = \text{g CN or } t \times 0.01302 = \text{g KCN}$$
$$(t_1 - 2\,t) \times 0.005808 = \text{g CNS or } (t_1 - 2\,t) \times 0.009718 = \text{g KCNS}$$
$$(T - t_1) \times 0.003546 \text{ g} = \text{Cl or } (T - t_1) \times 0.007456 = \text{g KCl}$$

13. Determination of Sulfuric Acid by Benzidine Hydrochloride*

$$1 \text{ l of } 0.1\ N \text{ NaOH} = \frac{H_2SO_4}{20} = 4.904 \text{ g } H_2SO_4$$

Benzidine, $C_{12}H_8(NH_2)_2$, is a weak organic base. It forms stable salts with strong mineral acids, of which the sulfate is characterized by its slight solubility, particularly in water containing hydrochloric acid. The base itself is neutral toward phenolphthalein. On account of being such a weak base, therefore, the aqueous solutions of its salts undergo hydrolysis. Thus benzidine hydrochloride is decomposed according to the equation:

$$C_{12}H_8(NH_2)_2{\cdot}2HCl + 2\,H_2O \rightleftarrows 2\,HCl + C_{12}H_8(NH_2)_2(HOH)_2$$

into hydrochloric acid and benzidine hydroxide, and the latter breaks down further into benzidine and water:

$$C_{12}H_8(NH_2)_2(HOH)_2 \rightarrow C_{12}H_8(NH_2)_2 + 2\,H_2O$$

In other words, an aqueous solution of benzidine hydrochloride behaves like a mixture of hydrochloric acid and benzidine, and the amount of acid present may be titrated with alkali, using phenolphthalein as an indicator.

There are two methods which have been used for the volumetric estimation of sulfuric acid by means of benzidine. Müller treated the *neutral* solution of the sulfate with a solution of benzidine hydrochloride of known acidity.

$$C_{12}H_8(NH_2)_2{\cdot}2HCl + Na_2SO_4 = 2\,NaCl + \underset{\text{Insoluble}}{C_{12}H_8(NH_2)_2{\cdot}H_2SO_4}$$

The precipitate of benzidine sulfate was filtered off and the filtrate titrated with a standard solution of alkali. The loss in acidity corresponded to the amount of sulfuric acid present. Raschig, on the other hand, recommends treating the neutral or acid solution of the sulfate with benzidine hydrochloride solution, filtering off the precipitated benzidine sulfate, washing it, and then suspending it in water and titrating the sulfuric acid with 0.1 N sodium hydroxide at 50°.

* W. Müller, *Ber.*, **35**, 1587 (1902); Müller and Dürkes, *Z. anal. Chem.*, **42**, 477 (1903); F. Raschig, *Z. angew. Chem.*, **1903**, 617 and 818; von Knorre, *Chem. Ind.*, **28**, 2; and Friedheim and Nydegger, *Z. angew. Chem.*, **1907**, 9.

Raschig prepares the reagent as follows: Triturate 40 g of benzidine with 40 ml of water and rinse the paste into a liter measuring-flask with about 750 ml of water. Add 50 ml of concentrated hydrochloric acid and dilute to the mark. Shake well. Soon the benzidine will all dissolve, forming a brown solution which may be filtered if necessary. When using as a reagent, dilute with 19 times as much water.

Procedure. — To the neutral or slightly acid solution of the sulfate, containing not more than 0.1 g of sulfate anions per 50 ml of solution, add the diluted benzidine solution in the cold, using 150 ml for each 0.1 g of sulfate ions. A crystalline precipitate of benzidine sulfate forms at once, which can be filtered as follows after standing 5 minutes.

Place a Witt perforated porcelain plate in a funnel of 200-ml capacity. The diameter of the plate should be about 40 mm on the top. Place 2 pieces of filter paper on this plate, about 46 mm in diameter. Insert the funnel in a rubber stopper and place in a suction bottle. Moisten the filters with water, apply gentle suction, and press the papers to the sides of the funnel so that a tight pad is formed of about 3-mm depth, which will not allow precipitate to get by. Pour the supernatant liquid through this filter, rinse the precipitate and mother-liquor into the funnel, and drain. Wash with 15 ml of water added in small portions. Place the precipitate and filter, without the porcelain plate, in an Erlenmeyer flask, add 50 ml of water, and shake the contents of the stoppered flask until a homogeneous paste is obtained. Remove the rubber stopper from the flask, rinse off with water, add a drop of phenolphthalein solution, heat to about 50°, and titrate with 0.1 N sodium hydroxide. When the end point is nearly reached, boil the liquid for 5 minutes, and then finish the titration.

Remark. — This method does not give good results in the presence of ferric salts, but this difficulty can be overcome by reducing the ferric ion with hydrazine hydrochloride. Not more than 10 moles of HCl, 15 moles HNO_3, 20 moles $HC_2H_3O_2$, 5 moles alkali salt, or 2 moles ferric iron should be present to 1 mole of H_2SO_4. A satisfactory determination of the sulfur in pyrite may be made by dissolving 0.5 g of the sample according to the Lunge method (see Pyrite), evaporating off the nitric acid, taking up the residue in a little hydrochloric acid, diluting to 500 ml and using 100 ml for the treatment with benzidine hydrochloride.

14. Determination of Sulfuric Acid by Hinman's Method*

1 l of 0.1 $\frac{H_2SO_4}{30} = \frac{98.08}{30} = 3.269$ g H_2SO_4

This method depends upon the fact that barium chromate is easily dissolved by dilute hydrochloric acid whereas barium sulfate is not; 1 l of cold water dissolves about 2 mg of $BaSO_4$ and 3 mg of $BaCrO_4$, but the latter salt dissolves easily in

* *Am. J. Sci. and Arts*, **114**, 478 (1877). Cf. Andrews, *Am. Chem. J.*, **2**, 567; Pennock and Morton, *J. Am. Chem. Soc.*, **1903**, 2265; Bruhns, *Z. anal. Chem.*, **45**, 573 (1906); Holliger, *Ibid.*, **19**, 84 (1910), and M. Reuter, *Chem. Ztg.*, **1898**, 357.

acid because $HCrO_4^-$ as an acid is comparable to H_2CO_3. If a solution of barium chromate in dilute hydrochloric acid is added in slight excess to a solution containing SO_4^{--} ions, $BaSO_4$ is precipitated; then upon neutralizing the solution the remainder of the barium is precipitated as $BaCrO_4$, leaving 1 mole of CrO_4^{--} in solution for each mole of SO_4^{--} originally present. After filtering, the dissolved chromium can be determined iodometrically (p. 619).

The method is rapid and capable of giving theoretical values in the analysis of sulfates containing less than 5 per cent of SO_3. By slightly varying the conditions, however, the results are influenced and the most favorable conditions are not always the same for different sulfates. The method, therefore, is suitable for routine work, but is not theoretically perfect.*

The results are likely to be high — (1) If the barium chromate contains any water-soluble chromate. Since the solubility of barium chromate in hot water is appreciable there will always be a positive error from this source, if the solution is filtered hot.

The results will be low — (1) If there is any reduction of chromate other than the desired reduction with iodide; this may be caused by the presence of too much hydrochloric acid during the first precipitation. (2) If any other chromate is precipitated with the barium chromate, such as basic ferric chromate. (3) If the solution is not acid enough during the treatment with iodide the reduction of the chromate is likely to be incomplete. (4) If the solution is hot, or contains an insufficient amount of iodide there is likely to be some loss of the iodine.

Prepare the barium chromate reagent by precipitating barium chloride with potassium chromate at the boiling temperature. Wash the precipitate with hot, dilute acetic acid and then with water till free from chromate. Dissolve 2–4 g of the dry salt in 1 l of normal hydrochloric acid. One milliliter should precipitate 0.63 mg to 1.2 mg of SO_3.

Procedure. — If the solution of the sulfate is acid, nearly neutralize it with caustic alkali solution. Dilute with water until not more than about 5 mg of SO_3 is present in 100 ml. Heat to boiling and slowly add a slight excess of the barium chromate reagent. Boil for 1 minute, or for 5 minutes if any carbonate was present.

To the boiling solution cautiously add pure $CaCO_3$ in small portions until present in slight excess (use ammonia if iron, nickel, or zinc is present). Cool to room temperature and bring to a definite volume in a 250-ml measuring-flask. Filter through a dry filter, reject the first 20 ml, and take 100 ml of the filtrate for the titration.

Add 2–3 g of potassium iodide and 10 ml of concentrated hydrochloric acid. Shake well and allow to stand 15 minutes. Then titrate slowly with 0.02 N sodium thiosulfate solution.

Remark. — When iron, nickel or zinc salts are contained in the solution, the acid present cannot be neutralized with calcium carbonate, because these salts when

* In some cases it is simplest to apply a correction factor. Thus Komarowsky *Chem. Ztg.*, **31**, 498 (1907) deducts 0.3 ml from the final buret reading. J. Lurie, at the Mass. Inst. Tech., was able to modify the directions so that correct results could be obtained with several sulfates.

boiled with calcium carbonate and a soluble chromate form insoluble basic chromates, so that too little chromic acid will be found in the filtrate corresponding to too little sulfuric acid. In such a case the neutralization is effected with ammonia, an excess being added, the solution is boiled until the excess is almost entirely expelled and is then filtered.

15. Determination of Phosphoric Acid. Method of Pincus

Principle. — If a neutral solution, or one slightly acid with acetic acid, is treated with uranyl acetate, a greenish white precipitate of uranyl phosphate is formed:

$$KH_2PO_4 + UO_2(C_2H_3O_2)_2 = KC_2H_3O_2 + HC_2H_3O_2 + \mathbf{UO_2HPO_4}$$

If at the same time ammonium salts are present, ammonium is contained in the precipitate:

$$KH_2PO_4 + UO_2(C_2H_3O_2)_2 + NH_4C_2H_3O_2 = KC_2H_3O_2 + 2\ HC_2H_3O_2 \cdot$$

The end of the precipitation can be determined by testing a drop of the solution on a porcelain tile with potassium ferrocyanide. A brown coloration is formed as soon as an excess of uranyl salt has been added.

To precipitate the phosphoric acid completely, it is necessary to titrate in a boiling-hot solution. However, as a solution of calcium phosphate will become turbid on boiling, owing to the formation of secondary calcium phosphate ($CaHPO_4$), it is best to precipitate the greater part of the phosphoric acid in the cold, then heat to boiling and complete the titration.

Requirements. 1. *Potassium Phosphate Solution.* — Dissolve 19.17 g (corresponding to 10 g P_2O_5) of pure, monopotassium phosphate in 1 l of water.

Confirm the concentration of the solution by evaporating 50 ml to dryness in a large platinum crucible, igniting the residue over the full flame of a Bunsen burner and weighing as KPO_3; also by precipitating another portion as magnesium ammonium phosphate and weighing as magnesium pyrophosphate.

Fifty milliliters of the solution correspond to 0.5 g P_2O_5 and should yield 0.8315 g KPO_3 and 0.7839 g $Mg_2P_2O_7$.

2. *Calcium Phosphate Solution.* — Dissolve 5.461 g of $Ca_3(PO_4)_2$, corresponding to 2.5 g P_2O_5, in a little nitric acid, dilute with water to a volume of 1 l, and test the concentration of the solution by means of the molybdate method (p. 391).

3. *Uranyl Acetate Solution.* — Dissolve about 35 g of uranyl acetate in a liter of water.

4. *Ammonium Acetate Solution.* — Dissolve 100 g of pure ammonium acetate and 100 ml of 6 *N* acetic acid, in enough water to make 1 l of solution.

5. *Potassium Ferrocyanide.* — The salt is used in the powdered form.

Procedure

(a) *Standardization of the Uranium Solution*

To 50 ml of the potassium phosphate, or calcium phosphate, solution add 10 ml of the ammonium acetate solution; run in the uranyl acetate solution from a buret until a drop of the solution will show a brown coloration when treated with solid potassium ferrocyanide upon a white porcelain tile. Then heat the solution to boiling, when a drop of

it will no longer react with the ferrocyanide. To the hot solution add more of the uranium solution, until the brown color is obtained once more.

If for the precipitation of the phosphoric acid contained in 50 ml of the potassium phosphate solution (0.5 g P_2O_5), T milliliters of the uranium solution were required, its concentration is $\frac{0.5}{T}$ grams P_2O_5 per milliliter.

For the analysis of alkali phosphates, standardize the solution against the potassium phosphate solution, but for the analysis of an alkaline-earth phosphate use the solution of calcium phosphate.

(*b*) *Determination of Phosphoric Acid in Alkali Phosphate*

The solution to be analyzed should be of about the same concentration as that of the potassium phosphate used for the standardization, and titrated in the same way. Phosphate solutions of different concentrations give different results by the titration.

(*c*) *Determination of Phosphoric Acid in Calcium Phosphate*

Dissolve 0.25 g of calcium phosphate in dilute nitric acid, add ammonia until a permanent precipitate is produced, and redissolve this in a little acetic acid. Add 10 ml of the ammonium acetate solution, and titrate the solution with the standard solution of uranyl acetate.

Remark. — In the presence of iron and aluminum this method will not give accurate results because the phosphates of these metals are insoluble in acetic acid. In such cases, filter the turbid acetic acid solution and determine the phosphoric acid in the filtrate by the above titration. Ignite the precipitate consisting of iron and aluminum phosphates, weigh, and, if it amounts to less than 0.01 g, assume half its weight to be P_2O_5; otherwise determine the phosphoric acid in the precipitate by the molybdate method.

16. Determination of Nickel by Potassium Cyanide*

This method, which permits the volumetric estimation of nickel with speed and accuracy even in the presence of iron, manganese, chromium, zinc, vanadium, molybdenum, and tungsten, depends upon the fact that nickel ions react with potassium cyanide in slightly ammoniacal solution, to form a complex anion $[Ni(CN)_4]^{--}$,

$$Ni(NH_3)_6Cl_2 + 4\,KCN = K_2[Ni(CN)_4] + 6\,NH_3 + 2\,KCl$$

* Cf. Campbell and Andrews, *J. Am. Chem. Soc.*, **17**, 126 (1895); Moore, *Chem. News*, **72**, 92 (1895); Goutal, *Z. angew. Chem.*, **1898**, 177; Brearley and Jarvis, *Chem. News*, **78**, 177 and 190 (1898); Johnson, *J. Am. Chem. Soc.*, **29**, 1201 (1907); Campbell and Arthur, *ibid.*, **30**, 1116 (1908); and Grossmann, *Chem. Ztg.*, **32**, 1223 (1908).

If the solution of the nickel salt contains a precipitate of silver iodide, produced by adding a known amount of silver nitrate and a few drops of potassium iodide solution, the turbidity will not disappear until all the nickel has entered into reaction with the potassium cyanide.

$$AgI + 2\,KCN = K[Ag(CN)_2] + KI$$

The titration is finished by adding just enough more silver nitrate to cause the precipitate of silver iodide to reappear.

Requirements. — 1. A *nickel solution* of known content. Dissolve 10 g of pure nickel in 125 ml of 6 N nitric acid, boil off the nitrous fumes, and dilute with water to 1 l at 20°.

2. A *silver nitrate solution.* Dissolve 5 g of silver nitrate in water and dilute to 1 l.

3. A *potassium cyanide solution.* Dissolve 15 g of pure potassium cyanide and dilute to 1 l.

4. A *potassium iodide solution.* Dissolve 10 g of potassium iodide in 100 ml of water.

Standardization of the Potassium Cyanide Solution. — To 10 ml of the nickel solution, accurately measured with a pipet, add ammonium hydroxide in slight excess, dilute to 100 ml, add 6 drops of potassium iodide solution and about 1 ml of silver solution from a buret, noting the reading of the buret before adding the silver solution. From another buret, slowly run in potassium cyanide solution, with constant stirring, until the silver iodide precipitate dissolves. Then very carefully add silver nitrate solution until a permanent turbidity is formed and dissolve this by careful addition of more potassium cyanide solution. Since the potassium cyanide solution decomposes slowly, this titration must be made every day that the solution is used.

Next determine the relative strengths of silver solution and potassium cyanide solutions. From a buret, add 30 ml of the latter, neutralize with ammonia, dilute, add potassium iodide, and titrate in exactly the same way as just outlined.

From this last titration in which a milliliters of silver nitrate were found equal to b milliliters of potassium cyanide, 1 ml of $AgNO_3$ solution $= \frac{b}{a}$ milliliters of KCN solution. If T milliliters of potassium cyanide and t milliliters of silver nitrate were used in the titration of 10 ml of nickel solution (= 0.1 g Ni) then

$$1 \text{ ml of KCN solution} = \frac{0.1}{T - \frac{b}{a}t} \text{ grams Ni}$$

Analysis. — To 100 ml of solution containing approximately 0.1 g of nickel, add ammonium hydroxide * and continue exactly as in the above standardization with pure nickel solution.

F. Sutton † states that, instead of working with two solutions, equally reliable results can be obtained by using a potassium cyanide solution to which a little silver nitrate has been added. Thus, to the above solution of potassium cyanide there may be added about 0.50 g of silver nitrate which is first dissolved in water by itself. If this solution is used for titrating a nickel solution to which potassium iodide solution has been added, a precipitate of silver iodide is formed at once which increases at first on adding the potassium cyanide-silver nitrate solution until all the nickel is converted into potassium nickelocyanide, but the precipitate eventually disappears upon the further addition of the solution.

Remarks. — Instead of titrating the potassium cyanide against a known nickel solution, the standardization may be accomplished with 0.1 N silver nitrate solution. In this case it is best to take as end point the formation of a slight turbidity on adding silver nitrate, rather than the dissolving of the precipitate with potassium cyanide. One milliliter of 0.1 N silver nitrate solution = 0.01302 g of KCN = 0.002934 g of Ni.

The method can be carried out in the presence of most of the other elements of the ammonium sulfide group. If a clear solution is not obtained on adding ammonium hydroxide, the addition of ammonium chloride sometimes helps. If copper is present in amounts not exceeding 0.4 per cent, the copper will replace almost exactly three-quarters of its weight of nickel. If chromium is present, the dark color due to presence of chromic salts may be obviated by adding to the original sulfuric acid solution a 2 per cent solution of potassium permanganate until a slight permanent precipitate of manganese dioxide is obtained, whereby the chromium is oxidized to chromic acid. Filter the solution, concentrate in a 400-ml beaker to about 60 ml, then treat with sodium pyrophosphate, as described below. The method is not applicable in the presence of considerable cobalt, the presence of which is betrayed by the solution assuming a dark color upon the addition of potassium cyanide, but when the amount of the latter does not exceed one-tenth the amount of nickel present, the titration can be carried out successfully and the results represent the amount of nickel and cobalt present.

Zinc causes trouble unless alkali pyrophosphate is added. The titration can be carried out in the presence of aluminum, iron, and manganese if citric or tartaric acid or sodium pyrophosphate is added.

The temperature of the solution should not be much above 20°, for in hot solutions the results are not concordant. The quantity of ammonia present should not be too great, because there is a tendency for ammonia to impede the reaction if more than a slight excess is present. Potassium cyanide containing sulfide cannot be used; the reagent should be the purest obtainable. The results are accurate. The

* If the addition of ammonia does not give a clear solution, a few cubic centimeters of ammonium chloride solution should be added.

† *Volumetric Analysis,* 8th edition, p. 252.

method has been modified so that it can be used to advantage for the determination of nickel in nickel steel.

17. Determination of Nickel in Nickel Steel

Dissolve 1 g of steel in a casserole with 10–15 ml of 6 *N* of nitric acid (*d.* 1.2), adding a little hydrochloric acid if necessary. After the steel has dissolved, add 6–8 ml of 18 *N* sulfuric acid, and evaporate the solution until fumes of sulfuric anhydride are evolved. Cool, add 30–40 ml of water, and boil the contents of the casserole until all the ferric sulfate has dissolved. Transfer the solution to a 400-ml beaker, filtering if necessary, and add 13 g of sodium pyrophosphate * dissolved in 60 ml of water at about 60°. The pyrophosphate solution must not be boiled, as this causes the formation of normal phosphate. The addition of the sodium pyrophosphate causes the formation of a heavy white precipitate of ferric pyrophosphate. Cool to room temperature, and add 6 *N* ammonia drop by drop, while stirring constantly, until the greater part of the precipitate has dissolved and the solution has assumed a greenish tinge. At this point, it should react alkaline toward litmus and smell slightly, but not too strongly, of ammonia. Now gently heat the solution, while stirring; the remainder of the pyrophosphate will dissolve, giving a perfectly clear light green solution. If the ammonia is added too fast, or the solution is not carefully stirred, a brownish color is likely to result, but this can usually be overcome by carefully adding a few drops of dilute sulfuric acid. Cool the clear solution to room temperature; add 0.5 ml of the standard silver nitrate solution and 2 ml of the potassium iodide. Titrate with potassium cyanide until the precipitate of silver iodide has disappeared, and finish by adding just enough more of the silver nitrate to cause the formation of a slight turbidity again.

18. Determination of Copper by the Potassium Cyanide Method †

Principle. — If an ammoniacal solution of a cupric salt is treated with potassium cyanide, the intense blue color gradually disappears. The reaction is essentially as follows:

$$2\,Cu(NH_3)_4^{++} + 7\,CN^- + H_2O = Cu_2(CN)_6^{----} + CNO^- + 2\,NH_4^+ + 6\,NH_3$$

The temperature of the solution, the ammonia concentration, and the quantity of ammonium salts present affect the reaction so that a given quantity of copper does

* Instead of using sodium pyrophosphate to prevent the interference of iron and other metals, many chemists use citric or tartaric acid. In this case the solution is dark colored and the end point is a little harder to detect.

† Cf. Steinbeck, *Z. anal. Chem.*, **8**, 8 (1869); Dulin, *J. Am. Chem. Soc.*, **17**, 346; A. H. Low, *Technical Methods of Ore Analysis.*

not always react with the same quantity of potassium cyanide. The potassium cyanide solution, therefore, must be standardized under exactly the same conditions as under which the analysis is carried out.

Standardization of the Potassium Cyanide Solution. — Dissolve 20 g of pure potassium cyanide in a liter of water. Weigh out 0.2 g of pure copper wire, or foil, into a 200-ml Erlenmeyer flask and dissolve in 10 ml of 6 N nitric acid. After the copper has dissolved add 25 ml of water and 5 ml of bromine water. Boil to expel the excess of bromine. Then add 50 ml of water and 10 ml of concentrated ammonium hydroxide, cool to room temperature by placing the flask in cold water, and add the potassium cyanide solution slowly from a buret, while constantly rotating the contents of the flask. When the solution has become a pale blue, dilute to about 150 ml and continue adding the potassium cyanide until the solution is just decolorized. The weighed amount of copper divided by the number of milliliters of potassium cyanide required gives the titer of the solution.

Low's Method for Analyzing Copper Ores. — Weigh out 0.5 g of a rich ore, or from 2 to 4 times as much of a low-grade ore, into a 200-ml Erlenmeyer flask and treat with 6–10 ml of concentrated nitric acid. Boil until nearly all the red fumes are expelled. If necessary, also add 5 ml of concentrated hydrochloric acid to decompose the ore and continue boiling for a short time. After cooling somewhat, add 14 ml of 18 N sulfuric acid and evaporate until dense fumes of sulfuric acid are evolved. Then, after allowing to cool again, add 25 ml of cold water and a drop of concentrated hydrochloric acid to precipitate any silver as chloride. Boil to dissolve the copper and ferric sulfates and filter off the precipitated lead sulfate and silicious residue. Wash the residue with hot water and receive the filtrate in a 150-ml beaker, taking care not to let the filtrate exceed 75 ml.

Place a piece of sheet aluminum, about 14 cm long and 2.5 cm wide and bent into a triangle, in the beaker. Cover with a watch glass, and boil the contents of the beaker for about 10 minutes, whereby nearly all the copper is deposited as spongy metal. Now remove the flame and wash down the sides of the beaker with cold water. To precipitate the last traces of copper and to prevent the oxidation of the fine deposit, add 15 ml of strong hydrogen sulfide water and decant the liquid through a 9-cm filter. Wash off the copper from the aluminum by means of weak hydrogen sulfide water into the flask in which the ore was dissolved and decant the liquid through the filter. Set aside the beaker containing the aluminum foil and some copper. The operation of filtering should take place without interruption and the filter kept well filled with liquid to prevent the oxidation of any pre-

cipitate upon it, which would cause it to dissolve and give a turbid filtrate. After washing the deposit 4 times, using in each case 20 ml of weak hydrogen sulfide water, allow the liquid to drain from the funnel, and then replace the beaker containing the filtrate with the flask containing the deposited copper. Cover the aluminum foil, to which some copper usually adheres, with 10 ml of 6 N nitric acid, heat nearly to boiling, and pour the hot acid through the filter. Replace the flask with the beaker containing the foil, and heat the contents of the flask until all the copper is dissolved and the greater part of the red fumes expelled. Again place the flask under the funnel, cover the aluminum foil in the beaker with 5 ml of strong bromine water, and pour this through the filter. Then wash the aluminum foil and the filter with hot water. Boil the solution to expel the excess of bromine, cool to room temperature, treat with 10 ml of strong ammonia, and titrate with potassium cyanide exactly as in the standardization.

19. Determination of Lead by the Molybdate Method*

Principle. — The lead is precipitated as molybdate from an acid solution and the termination of the reaction is recognized by testing a drop of the solution with a drop of tannin solution, which gives a yellow coloration when an excess of ammonium molybdate is present.

Requirements. — 1. A solution of ammonium molybdate prepared by dissolving about 4.25 g of ammonium molybdate in water, and diluting to 1 l.

2. A freshly prepared tannin solution containing 0.1 g of tannin in 20 ml of water.

Standardization of the Ammonium Molybdate Solution. — Weigh out 0.2 g of pure lead foil into a 200-ml Erlenmeyer flask, dissolve in a mixture of 2 ml concentrated nitric acid and 4 ml of water, and evaporate the solution nearly, if not quite, to dryness. Take up the residue in 30 ml of water, add 5 ml of concentrated sulfuric acid, shake, and allow the lead sulfate to settle completely. Filter and wash the precipitate with 3.5 N sulfuric acid. Drop the filter, together with precipitate, into an Erlenmeyer flask, add 10 ml of concentrated hydrochloric acid, and boil the liquid until the filter is completely disintegrated. Then, after adding 15 ml more of concentrated hydrochloric acid, and 25 ml of cold water, carefully add 25 ml of concentrated ammonia, whereby the greater part of the acid is neutralized. Drop a piece of blue litmus paper into the solution, add ammonia to slightly alkaline reaction, and then glacial acetic acid until the litmus paper turns red. Dilute to about 200 ml with hot water and transfer about two-thirds of the solution to a beaker. Add the ammonium molybdate solution to the

* Alexander, *Chem. Ztg.*, **16**, 181 (1892); Low, *Technical Methods of Ore Analysis.*

latter from a buret until a drop of the solution, brought in contact with a drop of the tannin indicator upon a white porcelain tile, gives a brown or yellow color. Pour in some more of the lead solution to the beaker and repeat the operation until only a few milliliters of the lead solution remain in the flask. Finally add the rest of the solution, and finish the titration by adding the molybdate solution two drops at a time. If t milliliters of molybdate are used in titrating a grams of lead the titer of the solution is

$$1 \text{ ml ammonium molybdate} = \frac{a}{t} \text{ grams lead}$$

Procedure. — Weigh out 0.5 g of the ore into a 200-ml Erlenmeyer flask, add 30 ml of $4N$ hydrochloric acid, and boil until all the hydrogen sulfide is expelled. If the ore should not dissolve completely by this treatment, add a little concentrated nitric acid and continue heating until the ore is completely decomposed. As soon as this has taken place. add 14 ml of $18N$ sulfuric acid, and evaporate over a free flame until dense vapors of sulfuric acid are evolved. Allow to cool, add 20 ml of water, and boil the liquid 15 minutes to dissolve all the anhydrous ferric sulfate.

After cooling, filter off the precipitated lead sulfate and silicious residue and wash with cold $3.5N$ sulfuric acid. The lead sulfate is often contaminated with calcium or barium sulfate, and before the titration it must be purified. To this end, rinse the precipitate by a stream of cold water into the original flask; add 5 g of pure ammonium chloride and about 1 ml of concentrated hydrochloric acid. By boiling, all the lead and calcium sulfates are dissolved, but the gangue, which is easily distinguished from either of the above salts, remains behind. Neutralize the solution with ammonia and treat with an excess of ammonium sulfide. Allow the precipitate to settle; filter and wash with hot water until the filtrate no longer gives a test for calcium when tested with ammonium oxalate. As the lead sulfide may be contaminated with some iron sulfide, rinse it again into the original flask, by means of as little hot water as possible, treat with 5 ml of $2N$ sulfuric acid, shake until the precipitate is well broken up, add 25 ml of strong hydrogen sulfide water, filter through the same filter as was last used, and wash with cold water. By this time it is safe to assume that the lead sulfide is free from all calcium and iron. Once more return the filter and precipitate to the original flask, dissolve by boiling with 5 ml of concentrated hydrochloric acid, boil, and then, when the hydrogen sulfide is practically all expelled, treat with 2–3 drops of concentrated nitric acid to remove the last traces of hydrogen sulfide. Now add

25 ml of cold water, and treat the solution exactly as in the standardization of the ammonium molybdate.

Remark. — The smelter chemists in the western part of the United States use a much more rapid method, which gives good results in the hands of an experienced operator, provided the lead content of the ore is greater than 15 mg

*Procedure.** — Dissolve the ore in hydrochloric acid or hydrochloric and nitric acids, and filter the solution while hot without diluting any more than to prevent the acid attacking the paper. Wash the residue rapidly with a hot solution of ammonium chloride until the washings show no blackening when tested with ammonia and a drop of ammonium sulfide. Make the filtrate just alkaline with ammonia and add a slight excess of ammonium sulfide. Heat to boiling, filter off the precipitated sulfides, and wash with hot water. (The alkaline earths may be determined in the filtrate if desired.) Dissolve the sulfides in hot, dilute nitric acid and catch the resulting solution in the same beaker in which the sulfides were precipitated. Add 7 ml of concentrated sulfuric acid, and evaporate the liquid until dense vapors of sulfuric acid are evolved. After allowing to cool, add 20 ml of water and boil the liquid to dissolve the anhydrous ferric sulfate. Filter off the precipitated lead sulfate, wash free from acid, dissolve in a slight excess of ammonium acetate solution,† and dilute with water. After heating to boiling, titrate the hot solution with ammonium molybdate.

The above procedure serves when alkaline earths are present; but when these are known to be absent, the original solution of the ore can be at once evaporated with sulfuric acid, the resulting lead sulfate dissolved in ammonium acetate solution and titrated without any purification.

20. Determination of Zinc by Potassium Ferrocyanide‡

The potassium ferrocyanide method for titrating zinc is very accurate but it requires some experience before an operator becomes skilled in its use. The end point of the reaction corresponds to the formation of $K_2Zn_3[Fe(CN)_6]_2$.

$$3\,ZnCl_2 + 2\,K_4Fe(CN)_6 = 6\,KCl + \mathbf{K_2Zn_3[Fe(CN)_6]_2}$$

* This method was obtained through the courtesy of Mr. Franklin G. Hills of the American Smelting and Refining Co.

† If too much ammonium acetate solution is used, a transitory end point is obtained in the subsequent titration. It is necessary to use a hot solution, which does not contain too much of the salt. See p. 187.

‡ The directions here given are based upon the procedure used in the laboratories of the New Jersey Zinc Co. at Palmerton, Pa.

After this point is reached, a slight excess of ferrocyanide will give a brown coloration when tested with dilute uranyl solution or ammonium molybdate on a spot plate. If the solution contains a very small quantity of iron, a little prussian blue is formed and the color changes from pale blue to pea green at the end point.

Potassium Ferrocyanide Solution. — Dissolve 32.31 g of pure ferrocyanide in water and dilute to 1 l; 1 ml of this solution should react with 7.5 mg of zinc.

Standardization. — Weigh out into 400-ml beakers several 0.3-g portions of pure zinc, weighing to 4 decimal places. Cover with water and dissolve in 20 ml of 6 N hydrochloric acid. When all the zinc has dissolved, neutralize with strong ammonia, make slightly acid with hydrochloric acid, and add 6 ml of 6 N acid in excess. Add 2 drops of ferrous sulfate solution containing 2.5 g $FeSO_4 \cdot 7H_2O$ per liter. This corresponds to about 0.03 mg of iron. Dilute with water to 200 ml, heat to boiling, and titrate as follows: Reserve one-quarter of the solution in a small beaker, to avoid the necessity of titrating to the right end point at once. To the hot solution add the ferrocyanide with vigorous stirring. The solution assumes a blue color, which should be quite pale and is due to the reaction of ferrocyanide with a very small quantity of ferric iron formed from the ferrous solution added. When an excess of yellow ferrocyanide is present, the blue color changes to a pale green. Add a little more of the ferrocyanide and pour in all but about 5 ml of the reserved zinc solution. Again add ferrocyanide till the end point is reached and about 0.5 ml more. Add the last of the reserved solution, wash out the beaker with hot water, and titrate with ferrocyanide dropwise until the blue color fades sharply to a pea green. This is the end point.

Repeat the standardization until an agreement within 2 parts in 1000 is obtained.

Analysis of the Ore. — Weigh out into a small beaker enough of the powdered ore to give approximately 0.6 g of zinc. Moisten with water and add 10 ml of concentrated hydrochloric acid. If sulfides are present it may be necessary to add 10 ml of concentrated nitric acid at this point. Digest on the hot plate at a temperature below the boiling point for 1 hour. Remove from the plate and wash down the sides of the beaker and the cover glass. Add 10 ml of 18 N sulfuric acid and evaporate to fumes. In the case of very silicious material it is well to break up the silica with a glass rod before adding the sulfuric acid. Cool and dilute to 50 ml with water.

If there is any indication of undecomposed mineral in the residue filter and wash the residue with hot water. Digest the residue with hot ammonium acetate solution to remove lead sulfate and treat the residue

with sulfuric and hydrofluoric acids (cf. Silicate Analysis). Then after the removal of the excess acid, fuse with potassium pyrosulfate, dissolve the melt in dilute sulfuric acid, and add the solution to that previously obtained.

The next step is to reduce the ferric salt and precipitate copper, bismuth, etc., by treatment with 1 g of 20-mesh aluminum powder at a volume of about 50 ml. If it was not necessary to test the residue for zinc, the treatment should precede the filtering of the lead sulfate and silica precipitate. Add 10 drops of saturated sodium thiosulfate solution, cover the beaker with a watch glass, and heat 20 minutes. This serves to reduce the iron and precipitate all the copper group metals except about 0.05 per cent of cadmium, which does no harm. Transfer the solution to a 200-ml measuring-flask. Make up to the mark, mix and filter through a dry paper. Reject the first 10 ml of runnings and take 100 ml for the titration. Transfer the solution to a tall, 400-ml beaker and neutralize with sodium hydroxide solution till a jelly is formed (of $Al(OH)_3$) and the acidity corresponds to about 2 drops of 20 per cent sulfuric acid. Use methyl orange as indicator. Add 3 ml of 5 per cent sulfuric acid, dilute to 200 ml, and introduce a stream of hydrogen sulfide into the cold solution for 40 minutes, at the rate of at least 8 bubbles per second. Allow the precipitate to settle for 15 minutes, filter, and wash with cold water.

Wash back the zinc sulfide precipitate into the beaker and rinse out the hydrogen sulfide tubing with 10 ml of concentrated hydrochloric in hot water. Run the acid through the filter and wash with hot water. Heat the acid until all the zinc sulfide has dissolved and all the hydrogen sulfide is expelled. Dilute with cold water to 150 ml, add concentrated ammonia until slightly alkaline, neutralize with hydrochloric acid, and continue as in the standardization of the ferrocyanide solution.

21. Determination of Lead and Arsenic in Commercial Lead Arsenate

Two methods for determining lead and three methods for determining arsenic in this important insecticide will be described, which are taken from the *Proceedings of the Official Agricultural Chemists of the United States.*

If the sample is in the form of a paste dry the whole of it on the water-bath to get the water content. Grind the residue to a fine powder and dry at 110–120° to constant weight. Use this for the following analyses.

(*a*) *Determination of Lead as Sulfate.* Dissolve 2 g of the dry powder in 80 ml of 2.5 N nitric acid. Heat on the water-bath until all the lead arsenate is dissolved. Transfer to a 250-ml measuring-flask and dilute

to the mark at 20°. To 50 ml of the solution, add 3 ml of concentrated sulfuric acid and evaporate till dense fumes of sulfuric acid are evolved. This is best accomplished by heating in a 250-ml Erlenmeyer flask. Allow to cool, cautiously add 50 ml of water and 100 ml of 95 per cent alcohol. Allow to stand several hours, then filter and wash 10 times with a mixture of 3 parts concentrated sulfuric acid, 200 of alcohol, and 100 of water by volume. Ignite and weigh as lead sulfate (p. 186).

Remark. — If the sample contains any alkaline earth, the lead sulfate will be very impure and should be purified as directed on p. 187.

(*b*) *Determination of Lead as Chromate.* Dissolve 0.6906 g of dry powder in 25 ml of 3 N nitric acid. Filter if necessary. Dilute to 400 ml, heat to boiling, and add ammonia water until a slight permanent precipitate is formed. Dissolve this precipitate with a little 1.5 N nitric acid and add 2 ml in excess. To the hot solution, add from a pipet 5 ml of 10 per cent potassium chromate solution. Allow the precipitate of lead chromate to settle, filter into a Gooch crucible, wash with hot water till free from alkali chromate, dry at 140–150°, and weigh as $PbCrO_4$. The weight of the precipitate in grams multiplied by 100 gives the percentage of PbO present.

(*c*) *Determination of Arsenic by Modified Gooch-Browning Method.* Take 100 ml of the nitric acid solution prepared as described in (*a*), add 6 ml of concentrated sulfuric acid, and evaporate to fumes. Cool, transfer to a 100-ml measuring-flask with cold water and make up to the mark at 20°. Mix thoroughly by pouring back and forth into a dry beaker, allow the precipitate to settle in the stoppered flask and then decant the clear solution through a dry filter. After rejecting the first runnings, take 50 ml of the filtrate; add 4 ml of concentrated sulfuric acid and 1 g of potassium iodide. Dilute to about 100 ml and boil until the volume is reduced to about 40 ml. In this way the arsenic acid is reduced to the trivalent condition and iodine is liberated. Do not carry the evaporation too far, or attempt to boil off the last traces of liberated iodine. Arsenic iodide is reddish and colors the concentrated solution very much the same as a little iodine does. It is volatilized if the solution is evaporated too far.

Cool the solution under running water, dilute to about 300 ml and carefully add sodium thiosulfate solution until all the free iodine is reduced to colorless iodide adding starch paste toward the end. At this dilution, the color of arsenic iodide is not apparent. To the acid solution add 15 g of anhydrous sodium carbonate in small portions and titrate with 0.1 N iodine solution. One milliliter 0.1 N I_2 solution = 0.003749 g of As.

Remark. — Inasmuch as iodine reacts with sodium hydroxide to form hypoiodite and iodide, it is generally recommended to finish the neutralization with sodium bicarbonate solution. This is unnecessary, however, because sodium bicarbonate is formed by the reaction between acid and the normal carbonate and as long as free carbon dioxide is present in the solution, there is no danger. The quantity of sodium carbonate added should be greater than 1 and less than 2 moles for each mole of sulfuric acid present, and 2–3 g of bicarbonate, formed from the normal carbonate, should remain unneutralized.

(*d*) *Determination of Arsenic by the Distillation Method.* Provide a 250-ml distilling-flask with a long-stem, 50-ml dropping-funnel and connect it to a 60-cm Liebig condenser. Connect the outlet of the condenser to a 500-ml Erlenmeyer flask by a short bent tube extending about 10 cm below the bottom of the 3-hole stopper which closes the flask. Through the middle hole in this stopper insert a 50-cm piece of straight tubing so that it reaches to within about 1 cm from the bottom of the flask and acts as a safety tube. Through the third hole introduce a twice-bent glass tube starting from just below the stopper and leading nearly to the bottom of a second 500-ml Erlenmeyer flask with a 2-hole stopper. Through the second hole insert a twice-bent tube leading to a 250-ml Erlenmeyer flask. Place 50 ml of water in the first flask, 100 ml in the second, and 50 ml in the third, and surround the first two flasks with cracked ice. The third flask acts merely as a trap, and no arsenic chloride should reach it.

Weigh 0.4–0.6 g of the dry powder and 5 g of cuprous chloride directly into the distilling-flask, taking care not to let any powder get into the distilling arm. Add 100 ml of concentrated hydrochloric acid from the dropping-funnel and start distilling. When the volume of liquid in the distilling-flask has been reduced to 40 ml, add 50 ml more of acid and again distil to 40 ml. Finally add 25 ml more of concentrated hydrochloric acid and distil until only 20 ml are left in the distilling flask. This procedure ensures the complete volatilization of all the arsenic as trichloride from 0.6 g of commercial insecticides.

After the distillation is completed, rinse out the connecting tubes and transfer the contents of the first two absorption flasks to a 500-ml measuring-flask, and make up to the mark at 20°.

To 100 ml of the mixed solution add 15 g of sodium hydroxide dissolved in a little water, and finish the neutralization by adding sodium carbonate until the solution is alkaline to methyl orange. Then add 2 g of sodium bicarbonate and titrate with iodine (p. 603).

(*e*) *Determination of Arsenic by the Potassium Iodate Method of G. S. Jamieson.** In a solution containing trivalent arsenic in the presence of 11–20 per cent of hydro-

* *J. Ind. Eng. Chem.*, 10, 290 (1918).

gen chloride, arsenic can be accurately titrated by means of potassium iodate solution (cf. p. 617):

$$2\,AsCl_3 + KIO_3 + 5\,H_2O \rightarrow 2\,H_3AsO_4 + KCl + ICl + 4\,HCl$$

Transfer 100 ml of the 500 ml of solution, obtained after distilling as in the previous method, to a 250-ml glass-stoppered bottle, add 6 ml of chloroform, and titrate with standard KIO_3 solution containing 3.244 g KIO_3 per liter. One milliliter of this solution reacts with 3 mg of As_2O_3. If more than 25 ml of the iodate solution is needed, add 10–15 ml more of concentrated hydrochloric acid before finishing the titration, in order to maintain the proper acidity. The end point is explained on p. 618.

To determine arsenic present as *arsenite* in any insecticide:

Weigh out 0.14–0.4 g of the powder, depending upon the arsenic content, into a 250-ml glass-stoppered bottle. Add 30 ml of concentrated hydrochloric acid, 20 ml of water, and 6 ml of chloroform. Titrate at once with the iodate solution. Titrate rapidly at first, while shaking the bottle so as to give a gyratory motion to the contents. When the iodine liberated during the first part of the titration has largely disappeared from the solution, insert the stopper, shake well, and from this point add the reagent slowly, shaking after each addition. Finally wait 5 minutes after the color is discharged from the chloroform to see if it returns.

22. Determination of Arsenic in Ores. Modified Method of Low-Pearce-Bennett

Of the finely powdered ore, take 0.5 g if the arsenic content is not over 10 per cent. If the ore is richer, take only enough to furnish 0.05–0.10 g of arsenic. Mix the ore with 2 g of anhydrous sodium carbonate and 1.5 g of potassium nitrate in a No. 8 porcelain crucible and sprinkle about 1 g of the fusion mixture on top. Cover the crucible and heat very slowly over a small flame, gradually raising the temperature until finally the full heat of a good burner is used for 10 minutes. Cool and extract with 200 ml of hot water. Filter and wash with hot water until all the soluble alkali salts are removed as shown by the litmus test for sodium carbonate. In this way all of the arsenic is obtained as alkali arsenate.

Make the solution distinctly acid with acetic acid and boil 10 minutes to remove carbonate and nitrite. Cool and add sodium hydroxide until the solution is basic to phenolphthalein. Discharge the color with a few drops of acetic acid and add 20 ml of 0.1 N silver nitrate solution. After the reddish brown precipitate of silver arsenate has coagulated sufficiently, filter and wash with cold water till the washings are free from silver. Dissolve the silver arsenate by pouring small portions of hot 3 N nitric acid through the filter, using about 10 ml of acid in all. Dilute and titrate the silver by the Volhard method. One ml of 0.1 N KCNS solution = 0.002499 g of As.

Remark. — This method gives excellent results in the commercial analysis of arsenide ores but chromium and phosphorus interfere as silver chromate and phosphate, etc., behave like the arsenate.

PART III

GAS ANALYSIS

The chemical analysis of gas mixtures is accomplished usually by measuring and rarely by weighing the individual constituents, so that it is customary to express the results in percentage by volume. But inasmuch as the volume of a gas is influenced to a marked degree by the temperature and pressure, it is necessary to reduce each measurement to standard conditions of temperature and pressure, and further to take care that these remain constant during the whole of the analysis. A volume of gas V measured over water at $t°$ C and B millimeters barometric pressure* is reduced to the volume which it would assume at 0° C and 760 mm pressure in a dry condition by means of the formula

$$V_0 = \frac{V(B - w)}{760\,(1 + \alpha t)}$$

In this formula, V_0 represents the reduced volume,† V the volume of the gas at $t°$ C and B millimeters pressure, w the tension of aqueous vapor, and α the expansion coefficient of the gas (= 0.003665).

As, however, $\alpha = \frac{1}{273}$, the above formula may be written as follows:

$$V_0 = \frac{V(B - w)\,273}{760\,(273 + t)}$$

Instead of reducing the observed volume to the standard conditions by computation, it can be effected mechanically by compression (see p. 352).

* Here is understood the barometer reading reduced to 0° C. The reduction is accomplished by means of the formula: $B_0 = \frac{1 + \beta t}{1 + \alpha t} \cdot B$, in which B_0 represents the reduced reading, B the actual reading at $t°$, α the expansion coefficient of mercury (= 0.000181), β the linear coefficient of expansion of glass (= 0.0000085). For most purposes, however, the reduction to 0° C can be made with sufficient accuracy by making the following deductions from the actual readings:

5°–12°	1 mm	21°–28°	
13°–20°	2 mm	29°–35°	

† Or volume under *standard conditions.*

The Collection and Confinement of Gas Samples

Since all gases diffuse rapidly into one another even when separated by porous solid bodies or liquids, it is evident that the collection of the sample and its preservation offers certain difficulties. If a gas is confined in a bell jar over water and thus kept out of contact with the air, it will be found that different results will be obtained in the analysis of the gas from day to day. The air gradually penetrates through the water into the bell jar and in the same way the gas within the jar gradually diffuses into the atmosphere. This process will continue until finally the composition of the gas both within and without the jar is the same. The rapidity of the diffusion depends upon the extent to which the gases are absorbed by the liquid which separates them. Those liquids which absorb the gases readily, allow them to pass through it rapidly, and consequently cannot be used for keeping the gases apart. Of all liquids, mercury is best suited for the purpose, because it absorbs only minimum amounts of the different gases.

Gases which combine chemically with mercury, such as chlorine, bromine vapors, hydrogen sulfide, etc., cannot, of course, be collected over mercury; it is best to collect them in dry glass tubes and to seal the latter by fusing together the open ends in case the gas cannot be analyzed immediately. Through glass there is no diffusion, so that gases may be kept unchanged in sealed tubes for years.

If the gas is to be analyzed within a few days after the time of collection, it can be kept in pipet-shaped tubes. The ends are closed by thick pieces of rubber tubing into each of which is inserted a piece of glass stirring-rod with rounded ends; where the rubber tubing comes in contact with the glass it should be fastened tightly with wires. It is not permissible to keep gases in such tubes for a considerable length of time, for rubber, particularly when it has become hard, permits the diffusion of gases to some extent.

For less accurate analyses, the gases can be collected over water which has been previously saturated with the gas to be analyzed, and the analysis must be made immediately afterwards.

From what has been said, it is evident that care must be taken in collecting and keeping the gas to be analyzed. We will now consider briefly a few practical examples.

(a) *Collection of Gases in Accessible Places*

1. Draw out the neck of a 200-ml flask somewhat and insert a glass tube. (Fig. 124.) Draw about 800 ml of the gas to be analyzed through the flask by means of suction. Then close the neck of the flask by means of a rubber cap and fuse the glass together.

(b) Collection of Gases from Inaccessible Places

Connect the rubber tubing G, Fig. 125, on one side with the aspirator A of about 30-l capacity and on the other with the source of the gas, and allow water to flow quickly from the aspirator. After 5 or 6 l have run out, the air is usually completely expelled from the rubber tubing and replaced by the gas to be analyzed, so that it is now ready for collecting the sample. For this purpose, turn the stopcock H 90° to the right, so that the vessel R, which is to receive the gas, is in communication with the outer air, and expel the air from it by raising the mercury reservoir N. Then turn back the stopcock to the position shown in the figure and fill R with the gas by lowering N. As the tubing between the T tube and the stopcock contained impure

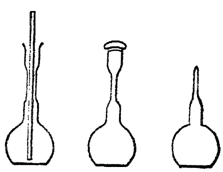

Fig. 124.

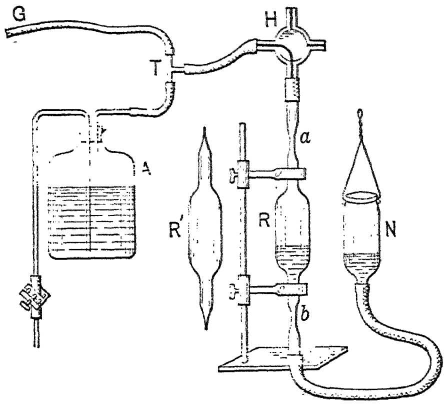

Fig. 125.

gas, again fill R with mercury and expel the gas into the air. After the process has been repeated 3 times, fill the receiver for the last time with the gas, close H, lower N so that the pressure in the tube is less than that of the atmosphere, and fuse together the ends of R first at a then at b. During this sealing of the tube, it should be removed from the ring-stand so that the tube can be revolved a little while being heated in the flame.

In sealing the tube, draw out the ends into a capillary as shown in R', Fig. 125.

If it is necessary to obtain the gas from places at a very high temperature, *e.g.*, from blast-furnaces, producers, etc., glass tubes would melt, and if ordinary iron tubes were not melted they would decompose the gas. In this case it is best to use the water-jacketed iron tube devised by St. Claire Deville and shown in Fig. 126 Cause cold water to run

into the outer condenser at a and to run out at b, and collect the gas, as described above, through the tube c. It is important that the water should run through the tube fast enough to keep the inner tube cold; otherwise the gas will be decomposed. By this means there is no difficulty in collecting gas samples from different heights of the glowing layers of coal in blast-furnaces or producers, or from smoke stacks.

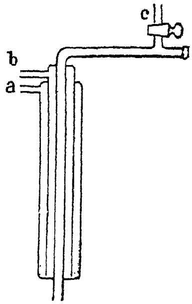

FIG. 126.

Collection of Gases Arising from Mineral Springs

Connect the receiver R with the funnel T by means of the rubber tubing q (Fig. 127). Fill all these parts of the apparatus with spring-water and allow the gas to ascend through the funnel as shown in the illustration. In order that the gas may pass from the funnel into the receiver, raise R, so that only the tubing p remains in the water, and lower the funnel as deep as possible, causing pressure enough to drive the gas over. Then close the tubing just above a by means of a screw-cock, place a beaker filled with spring-water under p, remove the apparatus from the spring, fuse together both ends of R with the blow-pipe. If the gas is to be analyzed within 2 or 3 days, the receiver may be closed by pieces of short rubber tubing each containing a short piece of glass rod with rounded ends. All such connections must be fastened by means of wires where the glass comes in contact with the rubber.

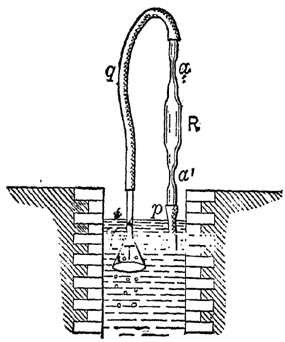

FIG. 127.

Collection of Gases Absorbed in Spring-water

Of the many different methods which have been proposed for the analysis of the absorbed gases in spring-water, the following is probably the most satisfactory.

Fill the flask A, Fig. 128, with spring-water up to its upper edge and immediately insert in the neck of the flask and press down the rubber stopper containing the tube L, which is fused together at the bottom but has an opening on the side at l. Raise the tube L so that the opening l is within the stopper, thus making an air-tight connection.

Now connect the bulb K with L, which is half full of distilled water and is connected with the capillary tubing C, although the latter is not yet connected with the measuring-tube B, as shown in the illustration. Raise the leveling-tube N until mercury begins to flow out of the right-angled capillary tube, then close the stopcock H. After this boil the water in the bulb K (which is held in an inclined position) for 3 minutes, meanwhile warming the capillary tubing connected with the measuring-tube. Unless this last precaution is taken, the capillary tubing is likely to break, particularly in winter. After the water in K has boiled vigorously for 3 minutes, remove the flame, quickly connect C with the measuring-tube B and securely fasten the rubber connection with wire. By boiling the water in K, a complete vacuum is produced in the bulb, so that the gas can be at once collected from the spring-water. For this purpose press down the tube L through the rubber stopper until the opening l comes just below its lower edge, lower the leveling-tube N, and open the stopcock H. At once there is a lively evolution of gas from the water in A, and this is subsequently maintained by warming the water. As soon as the eudiometer is full, close the stopcock and read the volume of the gas after bringing the mercury to the same level in N that it is in B. At the same time note the temperature of the water in the condenser M and read the barometer. Drive over the gas into the Orsat tube, O, containing potassium hydroxide solution (1 : 2), and allow it to remain there for the time being. Meanwhile continue boiling the water in A, and measuring the gas in B, etc., until finally no more gas can evolve from the spring-water. Drive over all the gas into the Orsat

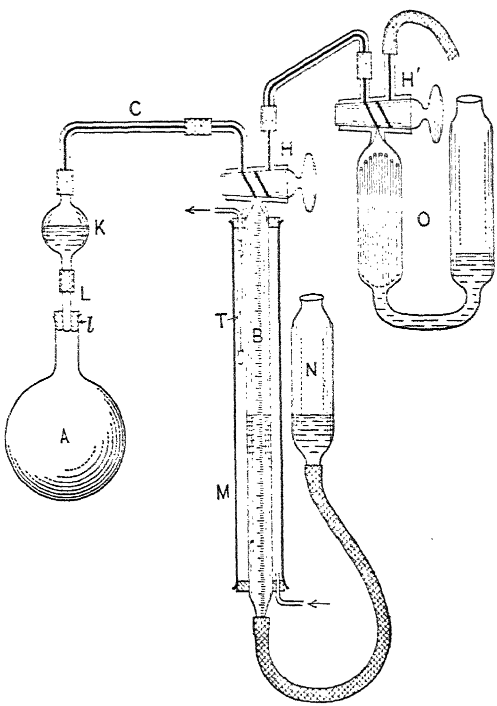

FIG. 128.

tube, after its volume has been noted; by means of the caustic potash, the carbonic acid is quantitatively absorbed. Again drive the unabsorbed gas over into *B* and read its volume. By correctly regulating the velocity of the current of water flowing through the condenser, it is easily possible to maintain a constant temperature throughout the whole of the experiment. The residual gas remaining after the absorption of the carbon dioxide consists usually of nitrogen, oxygen, and in some cases methane. Transfer it to the apparatus of Hempel, and analyze according to methods which will be described further on.

According to this method, the determination of nitrogen, oxygen, and methane gives exact results, but the apparent amount of carbon dioxide is sometimes too much and sometimes too little. If the water contains large amounts of bicarbonate in solution, the carbonic acid found will represent more than was originally present in the free state, for such substances are partly decomposed by boiling their aqueous solution. On the other hand, if only a little bicarbonate is present, the result will be too low, for it is not possible to remove all the free carbonic acid from a solution by boiling it in a vacuum.

Consequently, in all cases the free carbonic acid must be determined by computation. For this purpose determine the total carbonic acid in a fresh sample of the water, according to p. 357, and then if the composition of the solid constituents present is known, the volume of the free carbonic acid can be calculated.

Example. — 1000 g of Tarasper-Lucius water contain 7.877 g of total carbonic acid. Of this amount, a part is present in the water as bicarbonate, and the remainder is *free* carbonic acid. If from the total amount of carbonic acid the *combined* acid is deducted, the difference represents the amount of free carbonic acid present.

Calculation of the Carbonic Acid Present as Bicarbonate

This is obtained by multiplying the difference between the cations and anions (expressed in milli-equivalents) by the molecular weight of HCO_3, because the sum of the cations in every salt solution is equal to that of the anions present when both are expressed in milli-equivalents.

The gram equivalents are obtained by dividing the weight in grams of each element (or radical) by the respective atomic (or molecular) weight and multiplying by the valence.

By boiling 828.3 g of the water, 1868.9 ml of CO_2 were obtained at 8.4° and 651 mm pressure, containing only traces of nitrogen. This corresponds to 1851 ml per liter, at 0° and 760 mm pressure, which is more than the calculated amount, because by boiling some of the bicarbonate was decomposed.

CALCULATION OF THE MILLI-EQUIVALENTS

1000 *g of Lucas water contain:* *Cations*	*Wt. in mg*	
Potassium K^+	166	4.24
Sodium (Na^+)	3906	169.4
Lithium (Li^+)	9	1.30
Ammonium (NH_4^+)	13	0.72
Calcium (Ca^{++})	627	31.34
Strontium (Sr^{++})	9	0.20
Magnesium (Mg^{++})	190	15.60
Iron (Fe^{++})	6	0.20
Manganese (Mn^{++})	0.2	0.008
Aluminum (Al^{+++})	0.6	0.072

Sum of cations 223.08 milli-equivalents

Anions	*Wt. in mg*	*Milli-equivalents*
Chloride (Cl^-)	2400	67.7
Bromide (Br^-)	29	0.36
Iodide (I^-)	0.9	0.007
Sulfate (SO_4^{--})	1727	36.02
Hydrophosphate (HPO_4^{--})	0.08	0.018
Hydrocarbonate (HCO_3)	?	
		104.1 milli-equivalents

Sum of cations 223.1
Sum of anions 104.1

Bicarbonate ions 119.0 = 119 × 0.06101 = 7.262 g HCO_3 = 5.240 g CO_2.

CALCULATION OF FREE CARBONIC ACID

Total CO_2 = 7.877 g; combined CO_2 = 5.240 g; free CO_2 = 2.637 g = 1334 ml at 0° and 760 mm pressure.

If the amount of bicarbonate present is very small, the total amount of carbonic acid obtained by boiling the water is always too small. Thus with the thermal water of Baden, by boiling there was obtained:

Nitrogen	14.43 ml per liter
Carbon dioxide	112.12 ml per liter
	126.55 ml per liter

and from the analysis, the ree carbonic acid was computed to be 180.52 ml. The absorbed gas in the thermal water of Baden is, therefore,

Nitrogen	14.43 ml per liter
Carbon dioxide	180.52 ml per liter
	194.95 ml per liter

Remark. — With the above method of collecting the gas, it is difficult to prevent some water getting into the measuring-tube *B*, by means of which a small amount of the gas will be reabsorbed. This difficulty is avoided, however, if the flask shown in Fig. 129 is used to contain the water.

This flask is provided with a short tube blown into its neck near the top and connected by means of thick-walled rubber tubing with the mercury reservoir *R*. In order to determine the contents of the flask, make a scratch on the small tube about 4 cm from the neck of the flask, drive over the mercury just to this mark, and tightly close the rubber tubing by means of a screw-cock. Then empty the reservoir of mercury, and weigh the flask together with the stopper, glass tube *L*, rubber tubing, and what mercury remains above *Q*. Next fill the flask with water, press down the stopper to the mark in the neck of the flask, and raise the tube *L* until the lower opening *l* comes within the stopper. After drying the tube *L* with blotting-paper, weigh the flask and its contents. Etch its capacity upon the bulb of the flask.

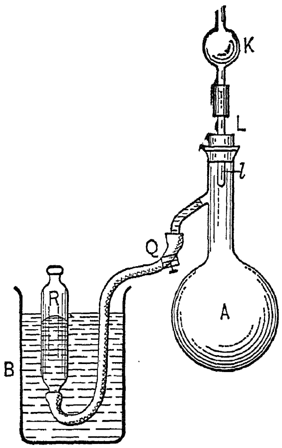

FIG. 129.

For the determination of the gases absorbed in a liquid, fill the flask *A* in the same way as in the determination of its capacity, connect the bulb-tube *K*, half filled with distilled water, with *L*, and connect *L* with a capillary tube as shown in Fig. 128. Remove the air from *K* and the capillary tubing by boiling the water in *K*, as described on p. 681, and then connect the capillary with the measuring-tube *B*, Fig. 128. Next connect the heavy rubber tubing with the reservoir as shown in Fig. 129, and place the latter in a beaker of hot water. Introduce the tube *L* into the neck of the flask until the opening *l* can just be seen, and expel the gas in the same way as described on p. 681, except that in this case the liquid is not allowed to rise so high in *K*. After three-quarters of an hour the gas will be completely expelled from the liquid. Drive over the last portions of the gas into *B* by lowering the leveling-tube *N* (Fig. 128), raising the mercury reservoir *R* (Fig. 129), and carefully opening the screw-clamp *Q*. A warm stream of mercury will then flow into the flask, expelling the gas into the measuring-tube. As soon as the liquid in *A* has been driven over as far as the stopcock *H*, immedi-

ately close H. Otherwise the procedure is the same as was described on p. 681.

To test the accuracy of this method, the author made a few determinations of the oxygen absorbed in the lake-water at Zurich, and the results were compared with those obtained by E. Martz in this laboratory by means of the method of L. Winkler (see p. 704).

OXYGEN IN 1 L OF ZURICH LAKE-WATER

Modified Petersson Method		Method of L. Winkler	
I	II	I	II
7.66 ml	7.74 ml	7.67 ml	7.75 ml

Collection of Gases Absorbed by Defibrinated Blood

The author has used for this purpose the apparatus shown in Fig. 130. The analysis is carried out as follows:

First fill the rubber tubing, which connects N' and A, with mercury by raising the leveling-tube N', and close the pinchcock h''. Then likewise fill the gas buret C with mercury by raising D and turning the stopcock h to the position shown in the drawing. By raising the leveling-tube N, fill the bulb K and the vessel A with mercury, and allow the mercury to flow into the funnel M up to the line a and then close the stopcock h. Pour the blood to be examined into M, lower N', and, by carefully opening h, allow the mercury to fall from M until it just reaches the stopcock h, which is then closed. Now fill M with blood to the mark b, open h, and suck down the blood until its upper level is exactly at the line a; then close h once more. Lower the leveling-tube N until a good vacuum is produced in A and the mercury level falls to near the bottom of K. When this is accomplished, the gas escapes from the blood so rapidly that all of A is filled with foam; after a few minutes, however, the effervescence subsides and all the blood collects in K. Then, raise the leveling-tube N until the blood reaches the cock h' and then close the latter. In this way the greater part of the gas absorbed is separated from the blood. Raise the leveling-tube N', open h'' so that the gas in A is under pressure, and by properly opening h and the buret stopcock, drive over the gas into the measuring-buret C; when this is accomplished, close h, lower N' until the mercury reaches the cock h'', which is then closed and h' opened. The blood again effervesces, but not so vigorously as before. Now surround the bulb K by water at 55°, which causes further effervescence

from the blood. As soon as the foam subsides, drive over again the gas into C and repeat the process of evacuating until the blood ceases to effervesce. Finally read the volume of the gas in C and note the temperature and pressure. Carry out the rest of the analysis as described on p. 717 or 724.

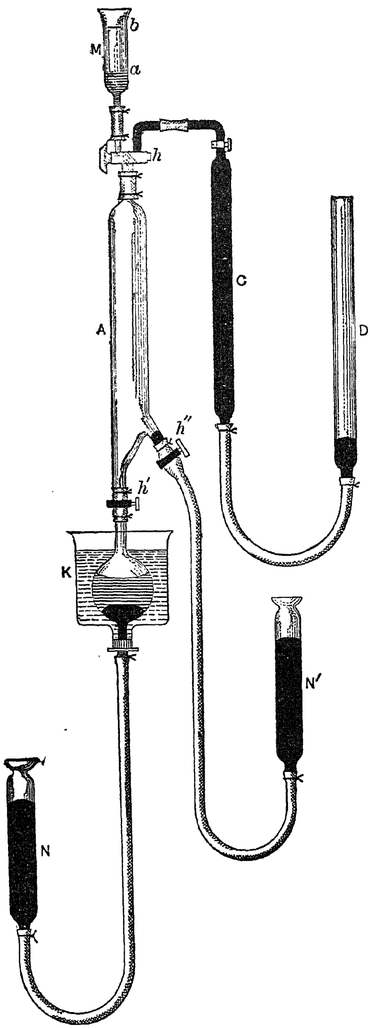

FIG. 130.

The Transference of Gases in Sealed Tubes to the Apparatus Used for the Analysis

Assume the gas to be contained in R, Fig. 131. Place a piece of thick-walled rubber tubing, containing a piece of heavy tubing r, over one of the short tubes connected with the three-way stopcock H. Turn the stopcock so that the rubber tubing is above it, and fill the tubing with mercury. Then turn H 180° toward the left so that the left and upper tubes communicate with one another. As soon as the mercury begins to run out, close the stopcock. Then introduce one end of R into the rubber tubing containing the mercury so far that its drawn-out point reaches within r, and fasten the rubber tubing securely by wiring, using annealed iron wire because copper or brass wire would be likely to become amalgamated with mercury. In a similar way, connect the other end of R with the rubber tubing filled with mercury of the leveling-tube N, and after this connect the stopcock H with the measuring apparatus W by means of the capillary tubing E. By raising the leveling-bulb K, expel the air from W and the capillary E, and

allow mercury to rise in the funnel T. Turn the stopcock H so that communication is established between R and W, and open the ends of R by pressing the capillaries against r and r'. Then, by raising N and lowering K, drive over the gas into W.

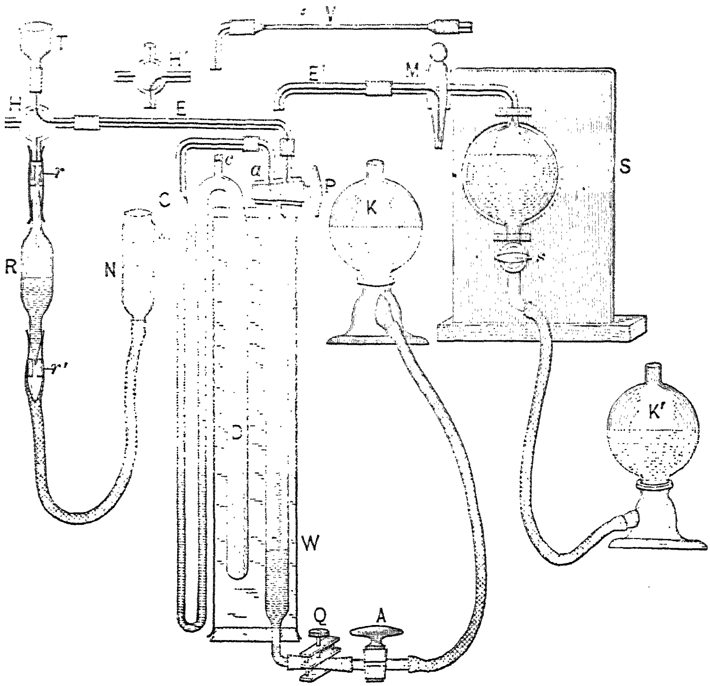

FIG. 131.

Calibrating Gas Measuring Vessels

When vessels are purchased to be used in measuring gases, the correctness of the calibrations should always be tested; the testing can be done with water or with mercury. The calibration with water is carried out in exactly the same way as was described for vessels to be used in measuring liquids (cf. pp. 465–471). The calibration by means of mercury will be illustrated by an example. Assume that it is desired to calibrate the apparatus shown in Fig. 132. The vessel must be thoroughly cleaned (cf. p. 465) and then placed in a vertical position as shown in Fig. 132 II. Connect the lower capillary a by means of thick-walled rubber tubing with a leveling vessel containing mercury, and cause the mercury to rise slowly in the vessel to a little above

the upper mark. Then close the stopcock, remove the leveling-tube together with the rubber tubing, and allow the mercury to flow out slowly until the highest point in the meniscus is exactly tangent to the horizontal plane through $\alpha'\alpha'$. To avoid a parallax error, take the reading with a telescope placed 2 or 3 mm away from the glass. Next allow the entire contents of the vessel, including the space in the stopcock, to run into a tared flask, and weigh to the nearest centigram. After determining the temperature of the mercury, its volume can be found by means of the table (top of p. 689) prepared by Schlösser.*

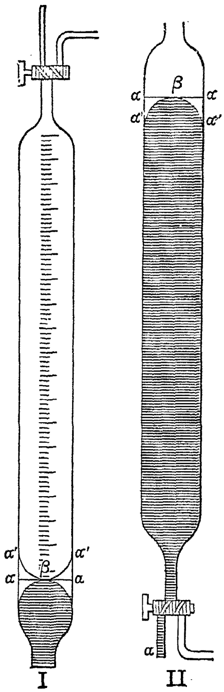

FIG. 132.

If the weight of the mercury at 20.3° amounted to 2025.26 g, then its volume corresponds to $\frac{2025.26}{13.5483} = 149.41$. Since, however, mercury forms a convex meniscus and the volume is desired up to the plane $\alpha\alpha'$, it is evident that the volume of mercury weighed did not include the space $\alpha'\alpha$–$\alpha\alpha'$, and, moreover, since the instrument is to be used in the reversed position, the error is really twice as much, as is evident from the inspection of Fig. 132 I. This is called the *double meniscus correction*. Its value is dependent upon the bore of the tube, as is shown by the table on p. 689.

If the diameter of the vessel in question is 20 mm, then the correction, according to the table, would be 4.016 g, and the true volume will be $\frac{2025.26 + 4.02}{13.5473} = \frac{2029.28}{13.5483} = 149.78$. The volume of this instrument, therefore, is 0.22 cm less than the intended 150 ml. The volume of the narrower parts of the tube can be found in a similar manner.

The diameter of the tube is best determined by filling with mercury up to a mark, then allowing it to run out until a lower mark is reached, weighing the escaped mercury, and measuring the distance between the two marks with a millimeter rule. If the weight of the mercury is p, the distance between the marks h, the temperature of the mercury 20.3° then the

$$\text{diameter} = \frac{p}{\cdot \times \pi \times 13.5483}$$

* Schlösser and Grimm, *Z. Chem. App.-Kunde*, **2**, 201 (1907).

WEIGHT OF 1 ML OF MERCURY IN AIR AT TEMPERATURES BETWEEN 15° AND 30°

Normal temperature 15°

Temperature °C	Weight of Mercury	Temperature	Weight of Mercury	Temperature	Weight of Mercury
15	13.5593	20	13.5489	25	13.5385
15.5	13.5583	20.5	13.5479	25.5	13.5374
16	13.5573	21	13.5468	26	13.5364
16.5	13.5562	21.5	13.5458	26.5	13.5353
17	13.5552	22	13.5447	27	13.5343
17.5	13.5541	22.5	13.5437	27.5	13.5332
18	13.5531	23	13.5426	28	13.5322
18.5	13.5520	23.5	13.5416	28.5	13.5312
19	13.5510	24	13.5405	29	13.5301
19.5	13.5499	24.5	13.5395	29.5	13.5291
				30	13.5280

TABLE OF MENISCUS CORRECTIONS*

Diameter of Tube in mm	Double Meniscus, Correction for Hg in mg	Double Meniscus, Correction for H_2O in mg = milliliters	Simple Meniscus Correction H_2O − Hg, in milliliters
3	76	12	3
4	108	20	6
5	174	31	9
6	314	44	10
7	550	61	10
8	790	81	11
9	1038	106	15
10	1288	134	20
11	1540	167	27
12	1796	204	36
13	2058	245	46
14	2326	289	59
15	2596	336	72
16	2872	387	88
17	3152	441	104
18	3436	499	123
19	3726	560	143
20	4016	624	164
21	4314	691	187
22	4614	757	208
23	4920	821	229
24	5230	881	247
25	5544	938	264
26	5864	991	279
27	6185	1042	293
28	6515	1090	308
29	6845	1135	315
30	7182	1179	324

* W. Schlösser. Private Communication.

In many cases it is sufficiently accurate to compute the diameter from the circumference of the tube and then subtract twice the thickness of the glass.

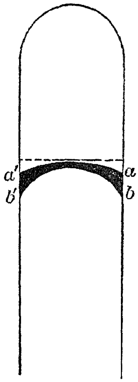

FIG. 133.

If it is desired to determine the total volume of a tube provided with stopcocks at both ends, the apparatus is weighed empty and then filled with mercury. In this case, it is obvious that no meniscus correction is necessary.

For a measuring vessel calibrated with water, when in a reversed position, the meniscus correction is obtained from the table on p. 689. If an instrument calibrated with water is to be used subsequently with mercury, the water meniscus in calibrating the reversed tube occupies a similar position to that of the mercury meniscus when the instrument is in use (see Fig. 132) but the mercury meniscus is not so deep as that of the water. The volume of the gas is therefore found as much too large as there is difference between the simple meniscus corrections for water and mercury. Thus if the volume of a gas-measuring instrument of 10-mm diameter is found by weighing with water to be 10.167, according to the table on p. 689, then if the instrument is to be used with mercury, the gas volume will be 10.167 − 0.020 = 10.147 ml.

Purification of Mercury. Lothar Meyer's Method*

The mercury used for gas-analytical operations must be purified. The principal impurities are copper, cadmium, zinc, and sometimes silver and gold. The base metals are removed most readily by allowing the mercury to run in a fine stream through about a meter of 8 per cent nitric acid. This is done in the apparatus shown in Fig. 134. First fill the bottom of the tube *B* with impure mercury and add the nitric acid. Then pour the mercury through the funnel *A*, the stem of which is drawn out to a capillary and bent to an angle of 60°. This causes the mercury to take a zigzag course as it flows slowly

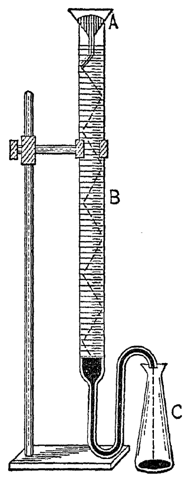

FIG. 134.

* *Z. anal. Chem.*, **2**, 241 (1863). C. J. Moore (*Chem. Ztg.*, **1910**, 735) has used a similar apparatus for purifying large quantities of mercury, but filters through buck-skin before allowing it to fall through the acid.

through the nitric acid. The dry mercury that first passes over into the flask *C* is impure and must be poured into the funnel and allowed to flow through the acid. In this way a fairly pure mercury is obtained which can be used as it is for most purposes. If the mercury is to be used for calibrating apparatus, it must be distilled.

For this purpose, Hulett's apparatus, shown in Fig. 135, can be used. Place the mercury in the long-necked flask *k* and connect with the receiver *V*. Cover the flask with a mantle of asbestos paper and heat on the sand-bath. Through the arm *a*, connect the receiver with a suction pump and introduce into the flask, through *b* and the long glass tube that ends in a capillary, a slow current of nitrogen (or carbon dioxide) which has been dried by passing over calcium chloride. Regulate the distillation so that the mercury condenses in the glass arm *s*, where it leaves the mantle of asbestos paper. About 150–200 ml of mercury can be distilled in an hour with this apparatus. Frequently, especially when the nitrogen used contains a little oxygen, the distilled mercury is covered with a thin coating of oxide. This may be removed by filtration. To filter the mercury, perforate the point of a paper filter several times with a needle, place the filter in a funnel and pour the mercury upon the filter. The pure metal runs through the holes in the paper while the impurity remains behind.

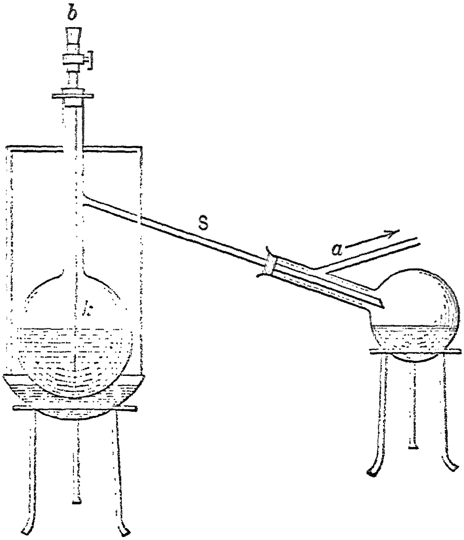

Fig. 135.

For the distillation of large quantities of mercury the apparatus* shown in Fig. 136 is suitable. Place the mercury in the container *R* (an inverted bottle with the bottom cut off). The tubing that rises above *R* is about 5 mm in diameter and that below is only 2 mm wide. The flask *K* has a capacity of about 300 ml and is fastened by a clamp to an iron rod attached to the wall of the room. The lower end of the

* Apparatus of M. Gony.

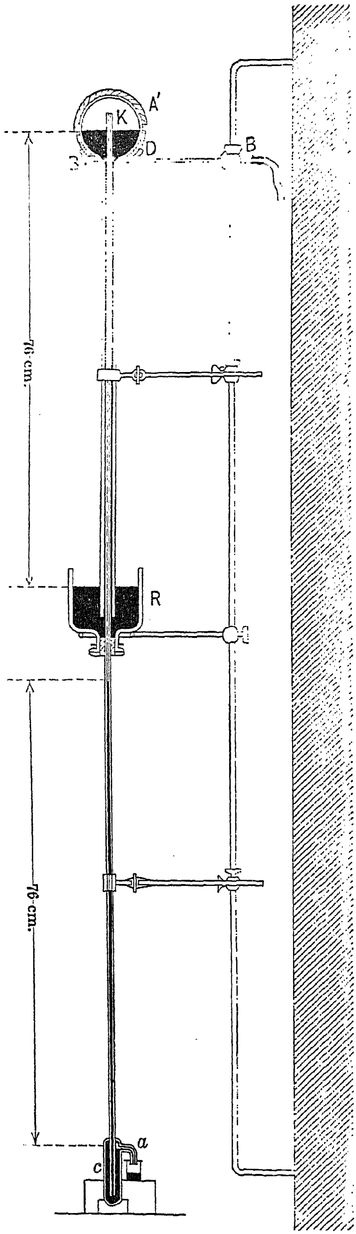

FIG. 136.

long neck of K reaches nearly to the bottom of R. By suction applied at a produce a partial vacuum in K. This causes mercury to rise in the tube from R into K. Light the ring burner at $B - B'$ upon which the flask K rests. Keep the suction working. The mercury soon boils and the vapor escapes into the tube but is condensed by the cooler liquid and falls in drops into the vessel c. As soon as all the air has been expelled from K, the lower half of the tube fills with mercury to a height corresponding to the atmospheric pressure. The vessel c also fills. At this point remove from a the rubber tubing that leads to the source of the suction and collect the dropping mercury in a flask.

To protect the flask K, wrap the lower half with wire gauze D and cover the upper half with a loose asbestos cap.

Subdivisions of Gas Analysis

According to the manner of determining the amount of gas, a distinction is made between:

1. *Absorption Methods.*
2. *Combustion Methods.*
3. *Volumetric Methods.*

In an *absorption method* the mixture of gases is treated with a series of absorbents. The difference in the volumes of the gas before and after it has been acted upon by each absorbent represents the amount of gas absorbed. The absorption

of the gas may take place in the measuring-tube itself, or, what is better, in separate absorption vessels.

In this way, the amount of carbon dioxide, heavy hydrocarbons (ethylene, benzene, acetylene, etc.), oxygen, and carbon monoxide may be determined in illuminating-gas, producer-gas, water-gas, or Dowson gas.

After the constituents capable of absorption have been removed, a gas residue is left consisting of hydrogen, methane, and nitrogen; the first two constituents are determined by combustion; the last is always determined by subtracting the total amount of other gases found from 100 per cent.

For a *combustion analysis* the unabsorbed constituents of the gas mixture are mixed with air, or oxygen, in more than sufficient amount to ensure complete combustion, and burnt in a suitable apparatus; the amount of combustible gas is determined by measuring the contraction, the amount of carbon dioxide formed, and the excess of oxygen.

Finally, if the gas evolved by means of a chemical reaction is measured and from the volume of the latter the weight of the body producing it is calculated, we have made use of what is called a *gas-volumetric* method. (Cf. Determination of Carbonic and Nitric Acids, pp. 350 and 403.)

DETERMINATION OF GASES

1. Carbon Dioxide, CO_2. Mol. Wt. 44

Density = 1.5290* (Air = 1). Weight of 1 l = 1.976 g
Molar volume = 22.26 l. Critical temperature = +31.5° C

Carbon dioxide is absorbed to a considerable extent by water; 1 vol. water absorbs: at 0°, 1.7967 ml CO_2; at 15°, 1.0003 ml CO_2; at 25°, 0.8843 ml CO_2, or in general

$$\beta\dagger = 1.7967 - 0.07761 \times t + 0.0016424 \times t^2$$

Absorbent. — Potassium Hydroxide Solution 1 : 2.

One milliliter of caustic potash of the above strength will absorb at least 40 ml of CO_2. Sodium hydroxide solution is not used on account of the difficult solubility of sodium bicarbonate.

* This number is the mean from the observations of Lord Rayleigh (1897) = 1.52909, Leduc (1898) = 1.52874, and Christie (1905) = 1.52930.

† β is called the absorption coefficient of the gas. This signifies the volume of gas, measured at 0° and 760 mm pressure, which 1 ml of a liquid at $t°$ will absorb when the pressure upon the surface of the liquid is 760 mm. If h milliliters of liquid, at $t°$ and B millimeters pressure, absorb V_t milliliters of the gas, then the absorption coefficient can be computed by the equation: $\beta = \frac{V_t}{h(1 + \alpha t)}$.

Small amounts of CO_2 may be absorbed by means of a definite volume of standard $Ba(OH)_2$ solution, and the excess of the latter titrated with $0.1\,N$ HCl, using phenolphthalein as indicator. (See p. 534.)

2. Carbonyl Sulfide, COS

Density = 2.0999 (Air = 1). Weight of 1 l = 2.7147 g. Molar volume = 22.13 l. Boiling point: −47.5°. Density of liquid COS, 1.0604. Critical

Vapor pressure of liquid COS in atmospheres: 0° = 14.5, 5° = 17.4, 22.8° = 20. 41° = 28.1, 67° = 36.7, 74° = 48.4, 94° = 62.9, 102° = ∞.

Formation. —

1. Hydrolysis of thiocyanic acid: $HCNS + H_2O = NH_3 + COS$.
2. Passing CO and CO_2 over boiling S: $CO + S = COS$.

$$6\,CO_2 + 9\,S = 3\,SO_2 +$$

3. Action of phosgene on metal sulfides: $CdS + COCl_2 = CdCl_2 + COS$.
4. Decomposition of thiocarbamate with 10 per cent hydrochloric acid:

$$\begin{array}{l} C{=}O \\ \;\;\diagdown NH_2 \end{array} + 2\,HCl = 2\,NH_4Cl + COS$$

5. Heating pyrite with potassium oxalate.

Carbonyl sulfide is colorless, odorless, and tasteless. It shows the following behavior toward reagents:

1. *Water* absorbs an equal volume of gas at ordinary temperatures. The solution is odorless and tasteless at first but soon hydrolyzes slightly: $COS + H_2O = CO_2 + H_2S$.

2. *Dilute caustic potash* solution does not absorb COS much better than water does. *Concentrated caustic potash* solution absorbs it, forming potassium carbonate and sulfide: $COS + 4\,KOH = K_2CO_3 + K_2S + 2\,H_2O$. The absorption is so slow that COS can be freed from CO_2 and H_2S by washing with potassium hydroxide solution. Alcoholic caustic potash absorbs COS quickly and completely.

3. *Ammonia.* Concentrated ammonium hydroxide solution absorbs COS slowly but completely, forming ammonium thiocarbamate: $COS + 2\,NH_3 = NH_2COSNH_4$ and in the presence of hydrogen peroxide, sulfate and carbonate are formed:

$$COS + 4\,H_2O_2 + 4\,NH_3 = (NH_4)_2SO_4 + (NH_4)_2CO_3 + 2\,H_2O$$

4. *Barium hydroxide* solution does not give a precipitate at once as with CO_2 but after about 1 minute a turbidity results.

5. Neutral or acid solutions of *silver nitrate* or *lead acetate* do not give precipitates of sulfide for about 8 minutes. In an ammoniacal solution of silver or zinc, or in a caustic alkali solution of lead salt, a precipitate of sulfide is formed immediately.

6. *Copper sulfate* in acid solution absorbs almost no COS.

7. *Iodine* in neutral or alkaline solution has very little oxidizing effect. Chlorine and bromine act only slightly at ordinary temperatures.

8. *Bromine* in alkaline solutions oxidizes COS readily: $COS + 4\,Br_2 + 12\,KOH = K_2CO_3 + K_2SO_4 + 8\,KBr + 6\,H_2O$.

9. *Fuming sulfuric acid* absorbs COS at room temperature without much oxidation; on being heated, sulfuric acid and CO_2 are formed.

10. *Triethyl phosphine* does not absorb COS (Difference from CS_2).

11. *Palladous chloride* absorbs COS quickly and quantitatively at 40–50°: $PdCl_2 + COS + H_2O = 2\,HCl + CO_2 + PdS$.

12. Mixed with 1.5 volumes of oxygen, COS burns with explosive violence and blinding light. In contact with glowing platinum COS decomposes smoothly into CO and S without change in volume.

Preparation of Pure Carbonyl Sulfide. Method of Klason*

The method is based upon the hydrolysis of potassium thiocyanate with dilute sulfuric acid:

$$KCNS + 2\,H_2SO_4 + H_2O = KHSO_4 + NH_4HSO_4 + COS$$

The reaction is not quite so simple as the above equation would indicate, for besides the products shown some CO_2, SO_2, CO, H_2S, HCN, CS_2, C_2H_5SH, and HCO_2H are formed.

Dissolve 195 g of potassium thiocyanate in 100 ml of water and pour the solution in a cooled mixture of 2460 g concentrated sulfuric acid and 1900 ml of water in a 2.5-l flask. The solution is pink at first, then violet, and finally yellow. The evolution of gas starts at 18° but soon becomes so violent that it is necessary to cool with ice. After the evolution of gas slackens, warm gently on the water-bath, but do not let the temperature rise above 30°. To purify the gas, pass it first through a saturated, aqueous solution of copper sulfate mixed with an equal volume of concentrated sulfuric acid, then through 33 per cent caustic potash solution; in this way H_2S, CO_2, HCN, and HCO_2H are removed completely. To remove CS_2, which is always present, pass the gas through a mixture of 1 part triethyl phosphine, 9 parts pyridine, and 10 parts nitrobenzene. Dry the COS by passing it through 2 worm tubes cooled with salt-ice mixture, then through a

* *J. prakt. Chem.*, **1887**, 64.

calcium chloride tube, and finally through 2 phosphorus pentoxide tubes. Liquefy the gas by cooling with ether and carbon dioxide snow and seal it into glass tubes.

To make use of the gas, transfer it to a small, perfectly dry gasometer and keep it over mercury. To fill the gasometer, first chill the contents of a sealed tube with ether and carbon dioxide snow, break off the point of the tube, and connect with the gasometer, using dry rubber tubing. Take the tube out of the freezing mixture and hold it loosely in cotton containing a little carbon dioxide snow. Reject the first quarter of the gas through the stopcock of the gasometer, letting it escape under a good hood.

Quantitative Determination of Carbonyl Sulfide

(*A*) *Determination of* COS *and* CO_2 *in the Presence of Each Other*

Absorb the two gases in an ammoniacal solution of calcium chloride; calcium carbonate and ammonium thiocarbamate are formed. Add neutral hydrogen peroxide, boil, filter off the calcium carbonate, carefully avoiding contamination from the carbon dioxide in the air, wash with hot water, dissolve in T milliliters of $0.1\,N$ hydrochloric acid, and titrate back with $0.1\,N$ sodium hydroxide solution (p. 514). The difference $T - t$ multiplied by 1.113 gives the volume of the original CO_2 (at 0° and 760 mm) together with that formed from the COS. Evaporate the filtrate to small volume, make acid with hydrochloric acid, and determine the sulfuric acid as barium sulfate (p. 415). If the weight of $BaSO_4$ is p grams then 94.8 p milliliters of COS were present, measured under standard conditions. It may be assumed, without serious error, that an equal volume of CO_2 was formed from it.

Remark. — This method of analysis is suitable for the determination of large quantities of COS and CO_2. If but little COS is present mixed with considerable CO_2, Dede* recommends passing 25 l of the gas through palladous chloride solution heated to 50°. The COS is decomposed quantitatively into an equivalent quantity of PdS. Filter off the precipitate, dissolve it in hydrochloric acid and potassium chlorate, and determine the sulfur as barium sulfate.

(*B*) *Determination of* COS, H_2S *and* CO_2 *in a Mixture*

First determine the hydrogen sulfide content by bubbling the gas through a measured volume of $0.1\,N$ iodine solution until it is nearly decolorized. Determine the excess of iodine by titration with sodium

* *Chem. Ztg.*, **1914**, 1075.

thiosulfate solution. If t milliliters of 0.1 N iodine were used in reaction with H_2S, then 1.108 t milliliters of H_2S were present, measured under standard conditions.

In a second equally large volume of the gas absorb the three gases in an ammoniacal solution of calcium chloride. Afterwards boil with hydrogen peroxide and continue the analysis as in Method *A*. Assume that t_1 milliliters of 0.1 N acid were neutralized by the calcium carbonate and that p grams of $BaSO_4$ was formed. Then

$$COS = (p - t \times 0.01167)\ 94.8 \text{ ml at } 0^\circ \text{ and } 760 \text{ mm}$$

$$CO_2 = t_1 \times 1.113 - (p - t \times 0.01167)\ 94.8 \text{ ml at } 0^\circ \text{ and } 760 \text{ mm}$$

The Heavy Hydrocarbons

Ethylene (Ethene), C_2H_4; Benzene, C_6H_6; Acetylene (Ethine), C_2H_2

3. Ethylene, C_2H_4.* Mol. Wt. 28.03

Density = 0.9738 (air = 1). Weight of 1 l = 1.256 g†
Molar volume = 22.27. Critical temperature = +9° C

Preparation of Ethylene. — One of the most satisfactory methods consists in treating an alcoholic solution of ethylene bromide with zinc dust:‡

$$r_2 + Zn = ZnBr_2 + C_2H_4$$

In the neck of a round-bottomed, short-necked, 200-ml flask insert a rubber stopper with 3 holes, carrying respectively a safety tube provided with mercury seal, a gas delivery tube, and a dropping funnel. In the flask place a sufficient amount of zinc dust, moistened with alcohol, and gently heat at the start by placing the flask in a bath of water at about 50°. From the dropping-funnel slowly introduce a mixture of 1 part ethylene bromide and 20 parts absolute alcohol. Pass the escaping gas first through olive oil, to remove a little ethylene bromide which is carried over mechanically, then through caustic potash solution, and finally through water; collect over mercury, for example, in the Drehschmidt pipet (Fig. 131, p. 687). The gas thus obtained is nearly pure, particularly if the mixture of ethylene bromide and alcohol has stood for some time over anhydrous sodium carbonate to remove traces of hydrobromic acid.

* And its homologues.
† T. Batuecas, *Helv. Chim. Acta*, **1**, 136 (1918).
‡ Gladstone and Tribe, *Ber.*, **7**, 364 (1874).

Absorption Coefficient for Water

One volume of water absorbs at 0° 0.256 ml C_2H_4; at 15° 0.161 ml C_2H_4; at 20° 0.149 ml C_2H_4; or in general, $\beta = 0.2563 - 0.009136\, t + 0.0001881\, t^2$.

Alcohol absorbs more ethylene; the general formula is $\beta = 3.5945 - 0.07716 \cdot t + 0.0006812 \cdot t^2$.

Absorbents. — 1. Fuming sulfuric acid* (with 20–25 per cent free SO_3), 1 ml absorbs 8 ml of C_2H_4. According to Bone†, oxygen is also absorbed appreciably, but hydrogen and nitrogen are not.

2. Bromine water.‡

With bromine, ethylene bromide, $C_2H_4Br_2$, is formed. If a standardized bromine water is used for the absorption, the amount absorbed can be determined by titrating the excess of bromine. This excellent method, proposed by Haber,§ is at present the best known for the determination of ethylene in the presence of benzene. (See p. 701.)

Ammoniacal cuprous chloride solution will also absorb ethylene.

4. Benzene, C_6H_6. Mol. Wt. 78.05

Under standard conditions, 78.05 g of benzene vapor occupy a volume of 22.39 l.

Benzene is readily soluble in alcohol, ether, carbon bisulfide, caoutchouc, ethylene bromide, bromine, and fuming sulfuric acid.

Absorbents. — Fuming sulfuric acid‖ and bromine water containing an excess of bromine. After the solution has been used once, the absorption is incomplete.

Inasmuch as benzene is neither brominated nor oxidized by bromine at ordinary temperatures, it was difficult to understand why bromine water should absorb it quantitatively. In fact, Berthelot¶ and Cl. Winkler** disputed it, but the results of Treadwell and Stokes†† have been confirmed by Haber. Haber suggested that the absorption of benzene by bromine was of a purely physical nature, and M. Korbuly‡‡ has shown that such is the case. Just as bromine can be removed from

* Ethionic acid, $C_2H_6S_2O_7$, and carbyl sulfate, $C_2H_6S_2O_7$ are formed.

† *J. Chem. Soc.*, **61**, 879 (1892).

‡ Treadwell and Stokes, *Ber.*, **21**, 3131 (1888).

§ Haber and Oechelhäuser, *Ber.*, **29**, 2700 (1896).

‖ Benzene sulfonic acid is formed.

¶ *Compt. rend.*, **83**, 1255.

** *Z. anal. Chem.*, **1889**, p. 281.

†† Treadwell and Stokes, *loc. cit.*

‡‡ *Inaug. Dissertation*, Zürich, 1902.

aqueous solution by shaking with benzene, so benzene can be removed by shaking with bromine, or even ethylene bromide and like solvents.

By means of highly concentrated nitric acid (*d.* 1.52) benzene is also absorbed; this solvent cannot be used in the analysis of gases containing carbon monoxide, for this gas is quantitatively oxidized to carbon dioxide by nitric acid of this strength, and is therefore removed with the benzene* when the acid vapors are neutralized by caustic potash solution.

Behavior of Benzene to Water

Benzene vapors are absorbed to a considerable extent by water and all aqueous salt solutions, a circumstance which must be considered when an exact gas analysis is to be made. To determine how much benzene is absorbed by water, M. Korbuly performed the following experiments:

Different amounts of air containing 3.16 per cent of benzene vapor were shaken in a Drehschmidt's pipet with the same amount of water (5 ml) until no more benzene was absorbed. He obtained the following results:

Experiment	Gas Taken in ml	Per Cent Benzene Present by Volume	Amount of Benzene Absorbed at the End of 3 Minutes
1	58.92	3.16	1.28 ml = 2.17%
2	61.14	3.16	0.80 ml = 1.31%
3	58.32	3.16	0.52 ml = 0.89%
4	59.86	3.16	0.44 ml = 0.73%
5	60.78	3.16	0.28 ml = 0.46%
6	59.88	3.16	0.08 ml = 0.01%
7	60.20	3.16	0.02 ml = 0.00%

Potassium hydroxide behaves similarly.

In the analysis of a mixture of carbon dioxide and benzene, it is customary to first remove the carbon dioxide by means of potassium hydroxide solution and then the benzene with fuming sulfuric acid or bromine. It is evident, then, that both of the results obtained will be inaccurate if a fresh solution of potassium hydroxide is used for the absorption of the carbon dioxide, for this will absorb not only the whole of the carbon dioxide, but in many cases nearly all the benzene. Accurate results may be obtained by using a solution of potassium hydroxide which has been saturated with benzene vapors.

* Treadwell and Stokes, *loc. cit.*

5. Acetylene, C_2H_2. Mol. Wt. 26.02

Density = 0.9087 (air = 1).* Weight of 1 l = 1.175 g
Molar volume = 22.03 l. Critical temperature = +37° C
Boiling point = −80.6° C

Acetylene is quite soluble in water; 1 volume of water at the ordinary temperature absorbs an equal volume of this gas. In amyl alcohol, chloroform, benzene, glacial acetic acid, and acetone it is much more soluble; thus 1 volume of acetone absorbs 31 volumes of acetylene.†

Preparation of Pure Acetylene

(a) Method of M. Bretschger‡

Pass the crude acetylene, prepared from calcium carbide and water, through an acid solution of copper sulfate, then through aqueous chromic acid, caustic potash, and finally over slaked lime; then subject to a fractional distillation. Pass the gas through a small bulb cooled by liquid air which causes the acetylene to solidify. Afterwards, by gently heating, evaporate off the acetylene and dry the gas by passing it through calcium chloride tubes.

(b) Method of M. Stahrfoss and P. A. Guye

Pass the impure acetylene, prepared from calcium carbide and water, through a solution of potassium permanganate, then through caustic potash solution and finally over phosphorus pentoxide. Freeze by means of liquid air and then fractionate.

The method of preparing acetylene by decomposing copper acetylide cannot be recommended, because the gas is then strongly contaminated with ethylene (C_2H_4) and vinyl chloride (C_2H_3Cl).

Absorbents. — Fuming sulfuric acid.§ By saturated bromine water, acetylene is absorbed rapidly in the cold, but 0.1 N bromine water containing hydrochloric acid absorbs acetylene so slowly that it permits the titration of ethylene in the presence of acetylene (see p. 747).

By means of ammoniacal cuprous chloride, acetylene is absorbed and forms red copper acetylide $(Cu_2C_2H_2)O$. This reaction is so characteristic that it is used for the

* M. Bretschger (*Inaug. Dissert.*, Zürich, 1911), M. Stahrfoss and P. A. Guye (*Arch. sci. phys. nat.*, 28, 1909). The mean of their two values is used.

† Hempel, *Gasanalytische Methoden.*

‡ *Loc. cit.*

§ $C_2H_4SO_4$ is formed.

Qualitative Detection of Acetylene

in gas mixtures. This test is best performed by the method of L. Ilosvay von Nagy Ilosva.*

Preparation of the Reagent. — Place 1 g of copper nitrate (chloride or sulfate) in a 50-ml measuring-flask and dissolve in a little water. To the solution, add 4 ml of concentrated ammonia (20–21 per cent NH_3) and 3 g of hydroxylamine hydrochloride. Shake the liquid until it becomes colorless, and immediately dilute with water up to the mark.

The Qualitative Test. — Place a little of the reagent in a 500-ml glass-stoppered cylinder and pass the gas to be tested for acetylene (illuminating-gas) over it until the color of the reagent becomes pink. Stopper the cylinder and shake. If acetylene is present, a beautiful red precipitate is immediately formed. Another method of making the test is to pass the gas through a small bulb-tube containing glass wool moistened with the reagent.

Remark. — If the reagent is placed under kerosene it can be kept for about a week, but if copper wire is added to the solution, it can be kept much longer. The solution is much less permanent when it is prepared from the chloride or sulfate, even when copper is added to it.

Separation of the Heavy Hydrocarbons from One Another

It has been attempted repeatedly to separate ethylene from benzene, but usually in vain. The separation as proposed by Berthelot, of absorbing the ethylene with bromine water and afterwards removing the benzene by means of concentrated nitric acid, is erroneous in every respect.† The method of Harbeck and Lunge‡ is correct in principle but very tedious, and the original modification of Pfeiffer§ always gives too high results.

Recently Pfeiffer|| has improved his method so that it gives the same results as that of Harbeck and Lunge.

Haber and Oechelhäuser,¶ on the other hand, have devised a method which is accurate and to be recommended.

Principle. — In one portion of the gas, the sum of the ethylene and benzene is determined by absorption with bromine water or fuming sulfuric acid, while in a second portion the gases are absorbed in titrated bromine water, and the excess of

* *Berichte*, **32** (1899), p. 2698.

† Treadwell and Stokes, *loc. cit.*

‡ *Z. anal. Chem.*, **16**, 26 (1898).

§ *J. f. Gasbeleuchtung und Wasserversorgung*, **1899**, 697, and *Ber.*, **29**, 2700.

|| See *Chem. Ztg.*, 1904 (884).

¶ *J. Gasbeleuchtung und Wasserversorgung*, **1896**, 804, and *Ber.*, **29**, 2700.

the latter is determined iodometrically. From the amount of bromine required the ethylene is calculated:

$$1 \text{ ml } 0.1\,N \text{ I} = 1.113 \text{ ml } C_2H_4 \text{ at } 0° \text{ C. and } 760 \text{ mm pressure}$$

As this analysis is performed in the Bunte buret, it will not be explained in detail until this has been described. (See p. 747.)

6. Oxygen, O = 16. Mol. Wt. 32

Density = 1.1053 (air = 1). Weight of 1 l = 1.4289 g
Molar volume = 22.39 l. Critical temperature = −119° C

Oxygen is only slightly soluble in water; according to the experiments of L. W. Winkler,* 1 l of water will absorb the following quantities of oxygen and nitrogen from air at 760 mm pressure:

ABSORPTION OF ATMOSPHERIC AIR BY WATER

Temperature	Oxygen	Nitrogen	Air
	ml.	ml.	ml.
0°	10.24	18.57	28.81
5°	8.98	16.45	25.43
10°	7.97	14.67	22.64
15°	7.16	13.29	20.45
20°	6.50	12.19	18.69
25°	5.93	11.31	17.24
30°	5.47	10.59	16.06
35°	5.11	9.92	15.03
40°	4.83	9.35	14.18
45°	4.58	8.93	13.51
50°	4.38	8.59	12.97
55°	4.22	8.31	12.53

From these data, the absorption coefficient of pure oxygen for water at 0–55° can be computed.

ABSORPTION COEFFICIENTS OF OXYGEN FOR WATER

Temperature		Temperature	
0	0.04890	30	0.02608
5	0.04286	35	0.02440
10	0.03802	40	0.02306
15	0.03415	45	0.02187
20	0.03102	50	0.02090
25	0.02831		0.02012

Oxygen can be determined by combustion or by absorption.

* *Ber.*, **34**, 1410 (1901).

Determination of Oxygen by Combustion

The determination of oxygen by combustion may be effected by exploding it with hydrogen (Bunsen) or by conducting a mixture of the two gases through a glowing platinum capillary (Drehschmidt), exactly as in the determination of carbon monoxide (cf. p. 708). In both cases the combustion takes place in accordance with the equation:

$$\underset{1\ \text{vol.}}{O_2} + \underset{2\ \text{vols.}}{2\,H_2} = \underset{0\ \text{vol.}}{H_2O}$$

Three volumes of gas, therefore, disappear for each volume of oxygen present. If the contraction resulting from the combustion of a mixture of oxygen and an excess of hydrogen is designated by V_C, then the amount of oxygen present $= \frac{1}{3}V_C$.

Determination of Oxygen by Absorption

The absorbents of oxygen are:

1. *Alkaline Pyrogallol Solution* (*Liebig*)

Mix 1 vol. of 22 per cent aqueous pyrogallol solution with 5–6 times as much 60 per cent potassium hydroxide solution. One milliliter of this solution absorbs 12 ml of oxygen.

At a temperature of 15°, or higher, the absorption takes place quickly; the oxygen in 100 ml of air will be absorbed in 3 minutes or less. At lower temperatures the absorption takes place less readily and at 0° the above quantity of oxygen cannot be absorbed completely in half an hour.

A pyrogallol solution of the above concentration will not evolve carbon monoxide during the absorption.

2. *Phosphorus* (*Lindemann*)

The absorption of oxygen by means of phosphorus takes place by simply allowing the gas containing the oxygen to remain over moist phosphorus. The formation of white clouds indicates the presence of oxygen, and their disappearance shows that the absorption is complete. A temperature of 15–20° is best suited for the absorption.

The oxygen is completely absorbed at the end of 3 minutes from 100 ml of air at this temperature. At lower temperatures the absorption requires more time, and at 0° more than an hour is necessary.

If the gas contains more than 60 per cent of oxygen, moist phosphorus will absorb none of it at the ordinary atmospheric pressures. In this case the gas must be diluted with nitrogen or hydrogen until a mixture

is obtained containing less than 60 per cent oxygen, or the gas must be allowed to act upon the moist phosphorus under diminished pressure. In the latter case, however, the phosphorus easily becomes heated enough to melt it and the reaction becomes too violent.

Oxygen is not absorbed by moist phosphorus if the gas contains traces of heavy hydrocarbons, ethereal oils, alcohol, or ammonia. According to Hempel* 0.04 per cent of ethylene, and according to Haber† 0.17 per cent, suffices to prevent completely the absorption of oxygen.

3. *Chromous Chloride*

Consult the paper by Otto von der Pfordten, *Ann. Chem. Phys.* **228**, 112.

4. *Copper*

Conduct the gas over glowing copper, or introduce it into a Hempel pipet containing rolls of copper gauze and an ammoniacal solution of ammonium carbonate.

5. *Sodium Hyposulfite,*‡ $Na_2S_2O_4$ (Franzen§)

An alkaline solution of sodium hyposulfite is an excellent absorbent for oxygen. The reagent may be prepared for use in the Hempel pipet by dissolving 50 g of the salt in 250 ml water and 40 ml of 60 per cent caustic potash solution. For absorption in the Bunte buret, the above solution is too concentrated; in this case 10 g hyposulfite in 50 ml water and 50 ml of 10 per cent caustic soda may be used.

The absorption takes place in accordance with the equation:

$$2\,Na_2S_2O_4 + 2\,H_2O + O_2 = 4\,NaHSO_3$$

Sodium hyposulfite has the advantage over other absorbents that the absorption is always complete at the end of 5 minutes.

Determination of Absorbed Oxygen in Water. Method of L. W. Winkler‖

1000 ml 0. $_3$ solution $= \frac{O}{20} = 0.8$ g $= 559.8$ ml oxygen at 0° and 760 mm pressure

* *Gasanalytische Methoden.*

† *Experimental-Untersuchung über Zersetzungen und Verbrennungen von Kohlenwasserstoffen*, Habilitationschrift, Munich, 1896.

‡ Not to be confused with sodium thiosulfate which is often called "hyposulfite" especially in the trade.

§ *Ber.*, **39**, 2069 (1896).

‖ *Ibid.*, **21**, 2843 (1888).

Principle. — If water containing dissolved oxygen is heated in a closed vessel with manganese hydroxide, the latter is oxidized to manganous acid according to the following equation:

$$Mn(OH)_2 + O = H_2MnO_3$$

The amount of oxygen taken up is determined iodometrically by adding hydrochloric acid and potassium iodide to the manganous acid and titrating the liberated iodine:

$$H_2MnO_3 + 4\,HCl = MnCl_2 + 2\,H_2O + Cl_2 \quad \text{and} \quad 2\,KI + Cl_2 = 2\,KCl + I_2$$

Reagents Required. — 1. *An approximately 4 N $MnCl_2$ solution* obtained by dissolving 400 g of $MnCl_2{\cdot}4H_2O$ in water and diluting to 1000 ml. The manganese chloride must be free from iron.

2. *Sodium Hydroxide Solution Containing Potassium Iodide.* — On account of the nitrite usually present in commercial sodium hydroxide, prepare the solution from sodium carbonate and calcium hydroxide. Siphon off the clear liquid and concentrate in a silver dish until its density is 1.35. In 100 ml of this solution, dissolve 10 g of potassium iodide.

A portion of the alkaline potassium iodide solution on being acidified with hydrochloric acid should not immediately turn starch paste blue, and, furthermore, large amounts of carbonate must not be present.

3. 0.1 N *Sodium Thiosulfate Solution.*

Procedure. — Take a glass-stoppered flask of about 250-ml capacity and determine its exact capacity by weighing it first empty and then filled with water at 20°. If the water to be analyzed is saturated with air, simply pour it into the flask; otherwise conduct the water through it for 10 minutes. By means of a pipet reaching to the bottom of the flask, introduce 1 ml of the alkaline potassium iodide solution and immediately afterwards 1 ml of the manganese chloride solution. Stopper the flask, shake, and allow to stand until the precipitate has settled. Then, by means of the long-stemmed pipet, add about 3 ml of concentrated hydrochloric acid and once more shake the contents of the flask. The precipitate dissolves readily with liberation of iodine; titrate the iodine with sodium thiosulfate in the usual way.

Remark. — The results obtained by this method agree closely with those obtained by boiling the water as described on p. 684.

7. Carbon Monoxide, CO. Mol. Wt. 28.00

Density = 0.96702 (air = 1). Weight of 1 l = 1.2502 g
Molar volume = 22.397 l. Critical temperature = −136° C

Preparation. — Heat concentrated sulfuric acid in a fractionating flask to a temperature of 140°–160° upon an oil-bath, and allow formic acid (*d.* 1.2) to drop into it:

$$HCOOH = H_2O + CO$$

To free the escaping gas from water and acid vapors, pass it first through a Liebig condenser, which leads to an empty flask to receive the condensed water, and thence into a concentrated caustic potash solution.

This method* yields about 60 l of carbon monoxide in half an hour, using about 500 ml of concentrated sulfuric acid. The method of Wade and Panting,† according to which very pure carbon monoxide can be prepared by allowing concentrated sulfuric acid to drop upon potassium cyanide, is not, according to Allner, a suitable process for preparing large quantities of the gas; because considerable potassium cyanide becomes coated with pyrosulfuric acid during the reaction, so that there is considerable danger involved in working with the residues.

By the action of hot concentrated sulfuric acid upon oxalic acid, it is very easy to prepare a mixture of equal volumes carbon monoxide and carbon dioxide; on account of the large amount of the dioxide, however, this method is less satisfactory than that of Allner.

The gas is only very slightly soluble in water:

ABSORPTION COEFFICIENTS OF CARBON MONOXIDE FOR WATER‡

Temperature	β	Temperature	β
0°..........	0.03537	30°........	0.01998
5°..........	0.03149	35°........	0.01877
10°..........	0.02816	40°........	0.01775
15°..........	0.02543	45°........	0.01690
20°..........	0.02319	50°........	0.01615
25°..........	0.02142	55°........	0.01548

‡ L. W. Winkler, *Ber.*, **34**, 1414 (1901).

In alcohol the gas is about 10 times more soluble than it is in water.

Its determination is effected either by absorption or by combustion.

Absorbents. — *Ammoniacal Cuprous Chloride.* Shake 200 g of commercial cuprous chloride in a closed flask with a 25 per cent solution of ammonium chloride, and to every 3 volumes of this mixture add 1 volume of ammonia, *d.* 0.91. In order that the solution may remain active, place a spiral of copper wire into the flask, long enough to reach from the bottom up to the stopper.

One milliliter of this solution will absorb 16 ml of carbon monoxide.

Formerly it was the almost universal custom to absorb carbon monoxide by means of a *hydrochloric acid* solution of cuprous chloride, but today this is not done for the following reasons. The absorption of

* W. Allner, *Inorg. Dissert.*, Karlsruhe, 1905.

† *J. Chem. Soc.*, **73**, 255.

carbon monoxide by means of cuprous chloride takes place according to the equation:

$$Cu_2Cl_2 + 2\,CO \rightleftarrows Cu_2Cl_2{\cdot}2CO^*$$

The compound $Cu_2Cl_2{\cdot}2CO$ is extremely unstable and can be formed only when there is a certain pressure exerted by the carbon monoxide, so that when the acid solution is used the absorption will never be quantitative. Further, if a gas free from carbon monoxide (nitrogen or hydrogen) is shaken with such a solution after it has been used several times, a part of the $Cu_2Cl_2{\cdot}2CO$ in solution will be decomposed according to the above equation in the direction of right to left, until the partial pressure of the carbon monoxide set free is sufficient to restore equilibrium. Consequently the volume of the gas will appear greater after it has been treated with the cuprous chloride solution than it was originally.

When an *ammoniacal* cuprous chloride solution is employed, the absorption of the carbon monoxide is almost quantitative, but after such a solution has been used repeatedly it will readily give up some of the gas, although not so readily as the solution of cuprous chloride in hydrochloric acid or calcium chloride.† It is advisable, therefore, to adopt the suggestion of Drehschmidt, and first absorb the greater part of the gas by means of an old solution of cuprous chloride, afterwards removing the last traces by means of a freshly prepared solution, or one which has been used but a few times.

Besides carbon monoxide, the ammoniacal cuprous chloride solution will absorb acetylene, ethylene, etc., so that these gases must be removed previously by means of fuming sulfuric acid or bromine water.

By long shaking with concentrated nitric acid (*d.* 1.5), carbon monoxide is completely oxidized to carbon dioxide, and the latter can be removed by treatment with potassium hydroxide solution.‡

Determination of Carbon Monoxide by Combustion with Air or Oxygen

The following reaction shows how carbon monoxide may be determined by combustion: $\underset{2\text{ vols.}}{2\,CO} + \underset{1\text{ vol.}}{O_2} = \underset{2\text{ vols.}}{2\,CO_2}$.

From the reaction it follows:

* The compound has been isolated in the solid state. According to W. A. Jones (*Am. Chem. J.*, **22**, 287) its formula is $Cu_2Cl_2{\cdot}2CO{\cdot}4H_2O$, but according to the experiments of C. v. Girsewald in the author's laboratory, the formula is $Cu_2Cl_2{\cdot}2CO{\cdot}2H_2O$.

† Cuprous chloride is soluble in a concentrated solution of calcium chloride, 1 ml of this solution absorbs 12–15 ml of CO.

‡ Treadwell and Stokes, *Ber.*, **21**, 3131 (1888).

1. The difference in the volume of the gas mixture before and after the combustion is for 2 vols. CO; $3 - 2 = 1$ and for 1 vol. CO $= \frac{1}{2}$. This difference is designated as the contraction, V_C. *The contraction caused by the combustion of carbon monoxide is, therefore, equal to half the original volume of* CO.

2. *The volume of the carbon dioxide formed is equal to the volume of the carbon monoxide originally present.* If, then, the carbon dioxide is determined by absorption with caustic potash, the volume of the carbon monoxide is at once obtained, provided no other combustible gas containing carbon is present at the same time.

3. For the combustion of 2 vols. of CO, 1 vol. of oxygen is necessary, and consequently *the amount of oxygen consumed is equal to half the volume of the carbon monoxide.*

Methods of Effecting the Combustion

The combustion of the carbon monoxide can be carried out in several different ways: (1) By explosion. (2) By conducting the gas over glowing palladium or platinum. (3) By conducting the gas over copper oxide.

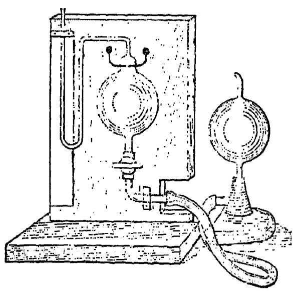

FIG. 137.

1. *Combustion by Explosion.* — Mix the gas with a sufficient amount of air in a measuring buret, such as is shown in Fig. 131, and connect the buret by means of the capillary E with the Hempel's explosion pipet shown in Fig. 137. Drive over the gas into the pipet so that the capillary is entirely filled with mercury, close the stopcocks of the capillary and of the explosion pipet, and cause an electric spark to pass between the two platinum points which are fused into the glass walls of the pipet; this immediately causes an explosion to take place. Afterwards once more drive the gas back into the measuring buret, and again determine its volume. The difference in volume before and after the explosion represents the contraction.

This most excellent method can sometimes lead to erroneous results. In practice, it is usually desired to determine the amount of combustible gas in a mixture containing nitrogen obtained after treatment with the different absorbents. If the amount of combustible gas present is too small in proportion to the amount of non-combustible gas, there will be no combustion whatsoever; on the other hand, if this relation is too large, a part of the nitrogen will be burnt to nitric acid (hydrogen is usually present). According to Bunsen, the combustion

is complete when 30 parts of combustible gas are present for each 100 parts of non-combustible gas. Consequently, if the explosion method is to be used for the analysis, the approximate composition of the gas must be known.

2. *Combustion by Conducting the Gas over Glowing Palladium or Platinum.* — This is the most certain of all methods for effecting the combustion, because it is entirely independent of the proportion of combustible gas present,* and there is no danger of any of the nitrogen being oxidized. The combustion is best effected, as proposed by Drehschmidt, by passing the gas through a thick-walled platinum capillary tube containing 3 palladium wires. Place the platinum capillary (Fig. 131, *V*) between the gas buret and the Drehschmidt pipet *S*, and heat it by means of the non-luminous flame of a Teclu burner. Repeatedly pass the gas through the glowing capillary until there is no further diminution in volume, showing the combustion to be complete. There is no danger to be feared from explosions even when pure detonating gas is passed through the platinum tube, and by this method CO, H, and CH_4 are completely oxidized. In the analysis of gases containing only small amounts of the above gases (*e.g.*, exhaust gases from gas-motors) the so-called fractional combustion is employed. By this means either hydrogen and carbon monoxide is oxidized while methane is not, or carbon monoxide is alone burned.

Fractional Combustion. — If, according to Haber, an absolutely dry gas mixture, consisting of considerable nitrogen and oxygen with little carbon monoxide, hydrogen, and methane, is slowly conducted (at the rate of about 700–800 ml per hour) through a glass U-tube 3 mm in diameter which contains a palladium wire 55 cm long, folded into 3 lengths of about 18 cm, then if the temperature of boiling sulfur is maintained, the hydrogen and carbon monoxide will be completely burned, while methane will escape from the tube in an unchanged condition. By connecting the U-tube with a weighed calcium chloride tube and then with 2 weighed soda-lime tubes (see p. 368) the increase in the weight of the U-tube will show the amount of water formed from the hydrogen, and the gain in weight shown by the soda-lime tubes corresponds to the amount of carbon dioxide formed from the carbon monoxide. If, after passing through the soda-lime tubes, the gas is passed through a combustion-tube filled with platinized asbestos, or copper oxide, which is heated to a dark red heat, the methane is quantitatively burned to water and carbon dioxide; the water can be ab-

* It is only necessary to make sure that a large excess of oxygen is present. Cf. Hempel, *Z. anorg. Chem.*, **31**, 447 (1902).

sorbed in a calcium chloride tube and the carbon dioxide in two soda-lime tubes, all three tubes being weighed before the gas is passed through them. In this way a check is obtained upon the accuracy of the determination, for the proportion of carbon to hydrogen found should be 1 : 4.

The combustion of carbon monoxide alone from a mixture of this gas with hydrogen, methane, and air can be effected satisfactorily as follows:

After the gas has been freed from CO_2, unsaturated hydrocarbons, and aqueous vapor, conduct it through a U-tube* containing 60–70 g of pure iodine pentoxide† heated to 160°; by this means the carbon monoxide is alone oxidized with liberation of iodine according to the equation $I_2O_5 + 5\ CO = 5\ CO_2 + I_2$.‡ If the gas is now conducted through 2 Péligot tubes containing potassium iodide solution, the iodine will be absorbed and can be titrated at the end of the experiment with $0.1\,N$ sodium thiosulfate solution.

One milliliter $0.1\,N$ $Na_2S_2O_3$ solution corresponds to 5.6 ml CO, measured under standard conditions.

If, after the carbon dioxide and water have once more been removed from the gas, it is passed through a combustion tube half filled with copper oxide and half with platinized asbestos, both heated to dark redness, the hydrogen and methane will be completely burned to water and carbon dioxide, which can be absorbed and weighed as before. From the amounts of each, the hydrogen and methane present in the gas can be calculated.

Qualitative Detection of Traces of Carbon Monoxide in the Air

If blood is diluted with water until the solution shows only a slight red color, it will give a characteristic absorption spectrum; 2 dark absorption bands appear between the D and E lines. If to this dilute blood solution a few drops of a concentrated, freshly prepared ammonium sulfide are added, the dark bands disappear, and instead a single broad band will appear at a place between the positions of the previous bands. Blood containing carbon monoxide behaves quite differently. When this gas is present, the blood takes on a rose color and the solution gives almost the same absorption spectrum as pure blood (the bands

* The U-tube is heated in a small paraffin-bath.

† Iodine pentoxide is prepared by heating iodic acid in a current of dry air at 180° until the water is completely removed.

‡ Nicloux, *Compt. rend.*, **126**, 746; Kinnicutt, *J. Am. Chem. Soc.*, **23**, 14; Marcelet, *Z. anal. Chem.*, **50**, 315 (1911); Morgan, *J. Am. Chem. Soc.*, **29**, 1589; V. Froeboese, *Z. anal. Chem.*, **54** (1915); Sinatt and Cramer, *Z. angew. Chem.*, **1915**, Ref. 9; A. Seidell and P. W. Meserve, *Hyg. Lab. Bull.* **92**, Washington, 1914; Moser and Schmidt, *Z. anal. Chem.*, **1914**, 217.

shift slightly toward the violet) but in this case *the two bands do not disappear on the addition of ammonium sulfide.*

To detect traces of carbon monoxide in the air, Vogel directs that a 100-ml bottle, filled with water, be emptied in the room containing the gas, and that 2–3 ml of blood, highly diluted with water, and showing only a very faint red color (although still giving the blood spectrum in a column as thick as a test-tube) be poured into the bottle and shaken for some minutes. To the solution a few drops of ammonium sulfide solution are added and the liquid is examined by means of the spectroscope. If the two bands are now visible, carbon monoxide is present. According to Vogel as little as 0.25 per cent of CO can be detected in this way.

Hempel has improved this method to a marked degree. He found that it was not possible to completely remove small amounts of carbon monoxide by shaking with the dilute solution of blood, and furthermore concentrated blood solutions could not be used because they foam so much. By using a living animal, its lungs furnish a better means of absorption, for the gas then comes in contact with undiluted blood. A mouse is placed between two funnels which are joined together by means of a broad band of thin rubber and the gas to be tested is passed through the funnels at a speed of 10 l per hour. At the end of 2 or 3 hours the mouse is killed by immersing the funnels in water and a few drops of its blood are taken from the region near the heart. In this way Hempel was able to detect with certainty as little as 0.032 per cent CO. With such small amounts of CO the live mouse showed no symptoms of poisoning; this was first apparent when 0.06 per cent of the gas was present. In the latter case after half an hour the mouse breathed with difficulty and lay exhausted on its side.

Potain and Drouin detect small amounts of carbon monoxide by passing the gas through a dilute solution of palladous chloride, whereby metallic palladium is precipitated:

$$PdCl_2 + CO + H_2O = 2\,HCl + CO_2 + \mathbf{Pd}$$

The solution is decolorized, or turns a pale gray, when large amounts of CO are present, but appears a light yellow in color when only traces are present.

In order to estimate better the decrease in color, Potain and Drouin filter off the deposited palladium and compare the color of the filtrate.

For the detection of small amounts of carbon monoxide, C. Winkler recommends a method which, as the author has found, will often lead to error. According to Winkler, the gas to be tested is conducted through a solution of cuprous chloride in a saturated solution of sodium chloride, afterwards diluting with 4–5 times as much water, causing

the precipitation of snow-white cuprous chloride. If this turbid solution is treated with a drop of sodium palladous chloride, a black precipitate of metallic palladium is obtained. Unfortunately, however, the palladium is often precipitated even in the absence of a trace of carbon monoxide, for cuprous chloride itself will readily reduce salts of palladium.

It is true, on the other hand, that at a definite concentration the reduction of the palladous chloride is only effected by means of carbon monoxide, but it is difficult to obtain always the right conditions, and herein lies the inaccuracy of the method. If the solution be too concentrated with respect to sodium chloride, even large amounts of carbon monoxide will fail to precipitate a trace of palladium, because in that case the solution contains not only copper but also palladium in the form of complex sodium salts: $Na_2[Cu_2Cl_4]$ and $Na_2[PdCl_4]$.

The sodium palladous chloride is not reduced by carbon monoxide and there is even less likelihood of the two sodium salts acting upon one another. If the solution be diluted with water, both salts break down according to the equations

$$Na_2[Cu_2Cl_4] \rightleftarrows 2\,NaCl + Cu_2Cl_2 \qquad Na_2[PdCl_4] \rightleftarrows 2\,NaCl + PdCl_2$$

and only when the palladium is in the ionic condition is it capable of entering into the reaction. The fact that the reduction of the palladous chloride is effected by means of CO at a concentration at which Cu_2Cl_2 is incapable of causing any reduction is easy to understand, for the gas, CO, comes in contact more readily with a sufficient number of palladium ions than does the difficultly soluble cuprous chloride.

8. Hydrogen, H. Mol. Wt. 2.016

Density = 0.06960* (air = 1). Weight of 1 l = 0.08998 g
Molar volume = 22.405 l. Critical temperature = −238° C

Hydrogen is practically insoluble in water.

ABSORPTION COEFFICIENTS OF HYDROGEN FOR WATER†

Temperature	β	Temperature	β
0°	0.02148	30°	0.01699
5°	0.02044	35°	0.01666
10°	0.01955	40°	0.01644
15°	0.01883	45°	0.01624
20°	0.01819	50°	0.01608
25°	0.01754	55°	0.01604

* Lord Rayleigh, *Proc. Roy. Soc.*, **53**, 1134 (1893).
† L. W. Winkler, *Ber.*, **24**, 99 (1891).

A. Determination by Absorption. Method of Paal and Hartmann*

Colloidal palladium, in the presence of a protective colloid, sodium protalbinate, is capable of absorbing an enormous quantity of hydrogen. The absorption takes place slowly but quantitatively. The absorbent can be regenerated, after each experiment, by treatment with oxygen or by adding an easily reducible organic substance. Paal and Hartmann made use of sodium picrate for this purpose; the picric acid is reduced to triaminophenol:

$$C_6H_2(OH)(NO_2)_3 + 9\,H_2 = C_6H_2(OH)(NH_2)_3 + 6\,H_2O$$

According to the experiments of Brunck† a solution of 2 g colloidal palladium and 5 g of picric acid dissolved in 22 ml of *N* sodium hydroxide diluted to 100–110 ml with water is a suitable absorbent. Such a solution can be purchased. The above quantity of reagent should absorb about 4 l of hydrogen; about 20–30 minutes, with repeated shaking, is required for the absorption. The reagent is useful for determining hydrogen in the presence of saturated hydrocarbons.

As soon as the efficiency of the absorbent is lost, rinse out the contents of the absorption pipet with water and add dilute sulfuric acid as long as any precipitate forms but avoid too much excess which tends to cause the palladium *sol* to go into solution as palladous sulfate, as a result of atmospheric oxidation. The precipitate of solid palladium and protalbinic acid also contains picric acid. Wash with water, which removes some of the acids but no palladium. Then suspend the mass in water and add sodium hydroxide solution, dropwise, until a colloidal solution is obtained. Finally add the proper quantity of sodium picrate and the absorbent is ready for use again.

B. Determination by Combustion

Mix a measured volume of the gas with more than half as much oxygen and burn the hydrogen by one of the following methods. The hydrogen can be determined by measuring the contraction in total volume.

$$\underset{\text{2 vols.}}{2\,H_2} + \underset{\text{1 vol.}}{O_2} = \underset{\text{0 vol.}}{2\,H_2O}$$

It is evident that by the combustion of 2 volumes of hydrogen, 3 volumes of gas will disappear (the water formed occupies a negligible volume). The contraction, therefore, is equal to $\frac{3}{2}$ the volume

* *Ber.*, **43**, 243 (1910).
† *Chem. Ztg.*, **1910,** 1313 and 1331.

of the hydrogen consumed. If the contraction is denoted by V_C and the volume of the hydrogen by V_H, then $V_C = \frac{3}{2} V_H$, and consequently $V_H = \frac{2}{3} V_C$.

In many cases the weight of the water formed is determined by absorption in weighed calcium chloride tubes; from the gain in weight, p, the volume of hydrogen is computed as follows: $\frac{22,405}{18.016} \times p = 1243.6 \times p$ milliliters hydrogen under standard conditions.

Combustion of Hydrogen, according to Cl. Winkler

The following method is employed frequently in *technical* analyses for the separation of hydrogen from methane.

Conduct a mixture of hydrogen and air over gently ignited palladium asbestos, by which means the hydrogen is quantitatively burned to water and the methane is not affected. Fig. 138 represents the apparatus required. A is the eudiometer and is connected by means of the capillary E, in which is found a short fiber of palladium-asbestos, with a Hempel pipet filled with water.

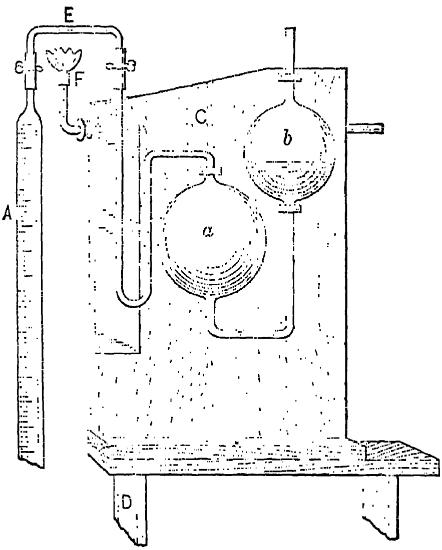

Fig. 138.

Heat the capillary, E, by a small flame F, at the place where the palladium-asbestos rests, to a temperature of about 300–400°, but not hot enough to soften the glass. After the gas, which is mixed with air,* has been passed back and forth through the capillary 3 times,† the combustion is complete. If the above-specified temperature is not exceeded, no trace of methane will be burned and the hydrogen determination will be accurate. It is difficult, however, to regulate this temperature

* If oxygen is used instead of air, some of the methane is sure to be oxidized. Cf. O. Brunck, *Z. angew. Chem.*, **1903**, 195.

† Pass the gas over the catalyzer so slowly that the palladium at the end toward the gas stream does not glow at all or only very slightly.

closely enough to prevent the combustion of some methane unless, as recommended by Haber, the tube is heated by means of sulfur vapor; the results are usually from 0.5 to 1 per cent too high.

Preparation of Palladium-asbestos. — Dissolve 3 g of sodium palladous chloride in as little water as possible, add 3 ml of a cold, saturated solution of sodium formate and enough sodium carbonate solution to make the solution alkaline. Then add about 1 g of soft, long-fibered asbestos which sucks up the whole of the liquid. Dry the mixture on the water-bath; by this means finely divided palladium is deposited uniformly through the asbestos:

$$Na_2PdCl_4 + HCOONa = 3\,NaCl + HCl + CO_2 + Pd$$

The hydrochloric acid formed by the above reaction is neutralized by the sodium carbonate. In acid solutions formic acid hardly reduces palladous chloride at all.

After the asbestos has thoroughly dried, soften the mass with hot water, place in a funnel and wash with hot water until the soluble salt is completely removed. Dry once more and preserve in a well-stoppered bottle.

Insert the palladium-asbestos fiber into the capillary tube as follows: Roll the fiber between the fingers to a little round wad, place it in the opening of the unbent capillary tubing, and by gentle tapping upon the table force it along to the center of the tube. Then bend the tubing as shown in the figure.

Remark. — Inasmuch as the palladium-asbestos is likely to become pushed into the capillary, it is perhaps more satisfactory to use a palladium wire wound into a spiral as catalyzer.

9. Methane, CH_4. Mol. Wt. 16.03

Density = 0.5545 (air = 1), Weight of 1 l = 0.7168 g
Molar volume = 22.36 l. Critical temperature = −82° C

Preparation. — Methane is conveniently prepared by a process analogous to that used in making ethylene* (cf. p. 697). Allow a mixture of equal parts methyl iodide and alcohol (*d.* 0.805) to act upon a zinc-copper couple which has been washed with alcohol.

$$2\,CH_3I + 2\,Zn + 2\,HOH = ZnI_2 + Zn(OH)_2 + 2\,CH_4$$

Prepare the zinc-copper couple by pouring a 2 per cent copper sulfate

* Gladstone and Tribe, *J. Chem. Soc.*, **45**, 154.

solution 4 times over granulated zinc, then washing with water, and finally with alcohol.

By allowing the mixture of methyl iodide and alcohol to drop upon the copper-coated zinc, a steady stream of methane is obtained at the ordinary temperature. Purify the gas by shaking it with fuming sulfuric acid, and then with caustic potash solution. It then contains about 98.4 per cent of CH_4 and about 1.6 per cent of nitrogen.

Methane can be prepared easily by the hydrolysis of aluminum carbide (Moissan).

$$Al_4C_3 + 12\,H_2O = 4\,Al(OH)_3 + 3\,CH_4$$

Wash the gas with water, then with fuming sulfuric acid, and finally with a mixture of colloidal palladium and ammonium picrate (see p. 713). Thus prepared, the gas is about 99.8 per cent pure.

Methane, also called marsh-gas or fire damp, is only slightly soluble in water.

ABSORPTION COEFFICIENTS OF METHANE FOR WATER*

Temperature	β	Temperature	β
0°	0.05563	30°	0.02762
5°	0.04805	35°	0.02546
10°	0.04177	40°	0.02369
15°	0.03690	45°	0.02238
20°	0.03308	50°	0.02134
25°	0.03006	55°	0.02038

In alcohol, the gas is about 10 times as soluble as it is in water.

Inasmuch as no satisfactory absorbent for methane is known, it is always determined by combustion. From the equation representing the combustion, $\underset{\text{1 vol.} + \text{2 vols.}}{CH_4 + 2\,O_2} = \underset{\text{1 vol.}}{CO_2} + \underset{\text{0 vol.}}{2\,H_2O}$, the following deductions can be made:

1. *Contraction.* — The contraction caused by the combustion of methane is equal to twice its original volume.

2. *Carbon Dioxide.* — By the combustion of methane an equal volume of carbon dioxide is produced.

3. *Oxygen Consumed.* — For the combustion of 1 volume of methane 2 volumes of oxygen are necessary.

* L. W. Winkler, *Ber.*, **34**, 1419 (1901).

Analysis of Illuminating and Producer Gases

The analysis of all such gases is best performed either by the method of Hempel* or that of Drehschmidt.†

Hempel's Method

Hempel's apparatus is shown in Fig. 131, p. 687. It consists of a eudiometer, *W*, with 0.2-ml graduations and connected by means of rubber tubing with the leveling-bulb *K*. The eudiometer is also connected with the compensation tube *D*, which in turn is connected with a manometer *C*; both the tubes *W* and *D* are surrounded by a cylinder containing water.

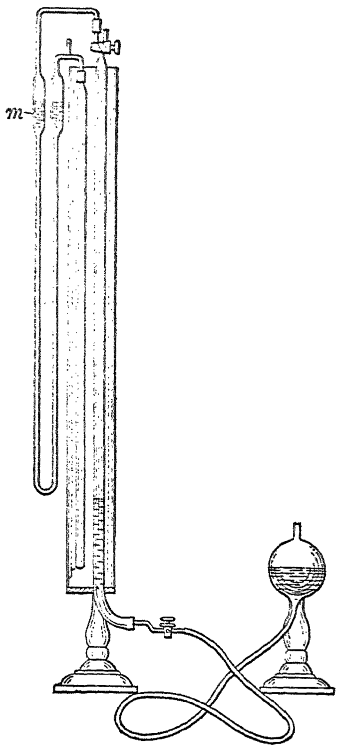

Fig. 139.

Calibration of the Apparatus. — First fill the manometer tube with mercury by raising the leveling-bulb *K* with the stopcock *p* in the position shown in Fig. 131, so that there is an open connection between *W* and *c*. Allow the mercury to pass over into *C* until the mark *mm* is reached. Then determine the volume of the manometer tube from the mark *m* to the point *a* (Fig. 131) as follows:

By carefully lowering the bulb *K* draw the mercury over into *C* exactly to the point *a* when the stopcock *p* is closed. Allow a little air to enter into the eudiometer through the right-hand capillary tube above *p* (the tube *E* should be withdrawn as in Fig. 139). Place the leveling-bulb *K* upon a solid support so that the mercury level in it is at the same height as in *W*, and with the stopcock *p* still open, read the position of the mercury in *W*. Close the stopcock, raise *K* a little, and turn *p* to the position shown in Fig. 131. By raising *K* still higher, drive the air over into the manometer tube *C* until the mercury has exactly reached the mark *m*, then close the

* *Gasanalytische Methoden* (1900).

† *Ber.*, **21**, 3242 (1888).

stopcock A (Fig. 131). Then adjust the position of the mercury by turning the stopcock p one way or the other, and once more read the position of the mercury in W. The difference between the two readings represents the volume of the tube between the marks m and a, an amount which must be added to all subsequent readings.

Introduce a drop of water at c, by means of a fine pipet, into the compensation tube D and either fuse together the end of the tube, or close with a cork stopper and make air-tight with sealing wax.

Procedure for the Analysis. — If the analysis is to be carried out on the spot, collect a large sample of the gas in a Drehschmidt pipet (Fig. 131 S). To accomplish this, connect the capillary tube E' by means of rubber tubing with the source of the gas, and turn the stopcock M so that the tube E' is in connection with the bulb of the pipet with the leveling-bulb and the stopcock s open. Fill the pipet with the gas, then turn the stopcock M so that it communicates with the outer air, and completely expel the gas from the pipet. In this way draw the gas in and out of the pipet at least 3 times to make sure that all foreign gas (air) is removed from the rubber tubing. Then collect the sample of gas and close the two stopcocks M and s.

In order to bring the gas to be tested from the Drehschmidt pipet into the eudiometer, connect the two instruments by means of the capillary E' (imagine the capillary E in Fig. 131 to be replaced by E') and firmly wire the rubber connections to the glass. Turn the stopcock M to the position shown in Fig. 131, raise the leveling-bulb K (after previously causing the mercury in the manometer-tube to reach to the point a) and fill the buret with mercury until it begins to flow from out of the tip of the key at M; then close the cocks A and p. Turn the cock M so that the pipet S and the buret W are in connection, raise K', open s, lower K, and open both p and A.

After about 40 ml of the gas have passed over into the eudiometer, close the cocks A and M, dip the key of the stopcock M (which must be entirely filled with mercury) into a beaker containing mercury, and suck the gas in the capillary into W by lowering K and opening A and p. As soon as the capillary E is entirely filled with mercury, close A, p and finally M.

Now determine the volume of the gas in W as follows: Open A and raise K so that the mercury in the bulb is a little higher than it is in W. After this open p and drive the gas over towards C until the mercury in both arms of the manometer tube is at about the same height; then close A immediately. Make the last fine adjustment of the mercury levels within the tubes by closing or opening the screw-cock Q. Read

the volume of the gas,* and to the reading add the correction corresponding to the volume between the marks M and a.

From this point the analysis begins.

1. Determination of Carbon Dioxide

With the stopcock p closed, turn the cock M as shown in Fig. 131, remove the Drehschmidt pipet, and replace by a second, clean pipet completely filled with mercury. On connecting the stopcock M with the rubber connector of the capillary E', it should be in the position shown in the drawing. By this means the mercury in the rubber tubing can flow out through the key. After wiring the rubber tightly to the glass, introduce 3–5 ml of caustic potash solution (1 : 2) through the key into the pipet M and wash out the alkali in the capillary with about 2 ml of distilled water and then with a little mercury; after this drive over the gas itself into the pipet. When the mercury has filled the whole capillary, both to the right and left of M, close A, p, and M. Raise the bulb K' so that extra pressure is placed upon the gas in the pipet and close s. Gently shake the pipet for 3 minutes without disconnecting it from the eudiometer, after which return the gas to W as follows: Open M, p, and A, lower K, raise K', and open s. When almost all the gas has been driven out of the pipet, close M, p, A, and Q, place the leveling-bulb on the table below, and K' upon the support (missing from Fig. 131, but shown in Fig. 139) upon which the pipet itself rests. Now open M, p, A, and s, and screw up Q a little so that the gas is very slowly sucked into the buret. As soon as the caustic potash solution has reached M, close it. Now remove the gas remaining in the capillary to the left of M by sucking mercury through the key of M into W. Finally read the volume of the unabsorbed gas in the same way as before. The difference between the two readings represents the amount of CO_2.

2. Determination of the Heavy Hydrocarbons or Illuminants

Remove the pipet containing the caustic potash solution and replace it with another containing fuming sulfuric acid.† Drive the gas over into the latter, and allow to stand with occasional passes to and fro,

* The reading is best made with the help of a small telescope, the ocular of which is provided with cross-hairs. For this purpose the telescope connected with a Bunsen spectroscope is suitable.

† In this pipet the bulb-tube K' is fused on to the absorption bulb, so that it is a little higher than the latter, in the same way as in the Hempel pipet (Fig. 142). Mercury is acted upon by fuming sulfuric acid.

for 45 minutes, then empty the pipet in precisely the same way as before. Return the gas to the pipet containing the caustic potash solution in order to remove the acid vapors, and finally transfer to the buret *W* and read its volume. The difference before and after the treatment with fuming sulfuric acid represents the sum of the heavy hydrocarbons or illuminants (C_2H_4, C_6H_6, C_2H_2, etc.). It is not usually customary to attempt to separate the benzene from the ethylene.

3. Determination of Oxygen

Carry out this part of the analysis in exactly the same way as the determination of the CO_2, but using an alkaline solution of pyrogallol in the absorption pipet (cf. p. 703).

4. Determination of Carbon Monoxide

The determination of carbon monoxide may be effected either by absorption with ammoniacal cuprous chloride or by simultaneous combustion with hydrogen and methane.

For the absorption method, the procedure is the same as in the case of the determination of the heavy hydrocarbons, *i.e.*, the absorption is effected in a pipet containing only ammoniacal cuprous chloride (no mercury). Shake the gas for 3 minutes with a solution of cuprous chloride which has already been used and then the same length of time with a fresh, or little used, solution (cf. p. 707). Before reading the volume of the unabsorbed gas, free it from ammonia vapors, by shaking with 4 *N* hydrochloric acid in a Drehschmidt pipet.

5. Determination of Hydrogen and Methane

After the removal of the carbon monoxide, the gas may consist of hydrogen, methane, and nitrogen. Add an excess of oxygen to this mixture (with illuminating-gas twice its volume, while with Dowson, water, and producer gas only a little more than half as much oxygen is necessary). Connect the eudiometer *W* with a Drehschmidt pipet entirely filled with pure mercury* using a Drehschmidt platinum capillary (Fig. 131, *V*), heat to bright redness with the non-luminous flame of a Teclu burner, taking care that the inner flame mantle does not come in contact with the platinum. Pass the gas mixture C times in a slow stream through the hot platinum tube, but take care that no mercury

* There must be no trace of caustic potash in the pipet because in that case CO_2 would be absorbed and an inaccurate result would be obtained. To make sure that all the alkali is removed, wash the pipet first with water, then with hydrochloric acid, and finally with water once more.

enters the tube. Then measure the volume of the burned gas without removing the platinum capillary, and determine the carbon dioxide by introducing some caustic potash into the pipet and shaking the gas with it; after 3 minutes' shaking, return the unabsorbed gas to the eudiometer, closing the stopcock M as soon as the caustic potash solution reaches it.

Calculation of Hydrogen and Methane

Assume V milliliters of gas to be taken for the analysis. The residue remaining after the absorption of the CO_2, C_nH_{2n}, O_2, and CO is mixed with oxygen and burned. The contraction produced is V_C and the CO_2 formed amounted to V_K.

It was shown on p. 716 that the volume of the methane is equal to the volume of the CO_2 formed, V_K, and in percentage: $\frac{V_K}{V} \times 100 =$ per cent CH_4.

Since by the combustion of 1 volume of CH_4 2 volumes of gas disappear, it is evident that by the combustion of V_K milliliters of CH_4 the contraction will amount to $2\ V_K$.

If the latter value be subtracted from the total contraction V_C, the difference represents the contraction caused by the combustion of the hydrogen present $(V_C - 2\ V_K)$, and two-thirds of this represents the amount of hydrogen. Therefore $200\ \frac{(V_C - 2\ V_K)}{3\ V} =$ per cent H.

Determination of Carbon Monoxide, Methane, and Hydrogen by Combustion

After the absorption of the CO_2, C_nH_{2n}, and O_2, the residual gas consists of CO, CH_4, H_2, and N_2. Add a measured volume of oxygen* explode the mixture, and determine both the contraction, V_C, and the carbon dioxide formed, V_K. After this determine the unused oxygen by absorption with alkaline pyrogallol solution. If the excess of oxygen is subtracted from the amount originally added, the difference will give the amount of oxygen necessary for the combustion, V_O.

* The purity of the oxygen must be tested before the analysis, because the commercial product almost always contains nitrogen. To a measured volume of nitrogen add a definite amount of oxygen, as otherwise the amount of the residual gas might be too small to fill the manometer tube between the marks a and m (Fig. 131). Prepare the nitrogen by allowing air to stand over phosphorus in a Hempel pipet. (Cf. p. 703.)

If the volume of CO is denoted by x, the CH_4 by y, and finally the H_2 by z, the following three independent equations hold true:

$$1.\ V_C = \tfrac{1}{2}x + 2y + \tfrac{3}{2}z$$
$$2.\ V_K = x + y$$
$$3.\ V_O = \tfrac{1}{2}x + 2y + \tfrac{1}{2}z$$

and from these equations

$$x = \tfrac{4}{3}V_K + \tfrac{1}{3}V_C - V_O = CO^*$$
$$y = V_O - \tfrac{1}{3}(V_K + V_C) = CH_4$$
$$z = V_C - V_O = H_2$$

Analysis according to H. Drehschmidt†

The apparatus of Drehschmidt, like that of Hempel, consists of the gas-buret B and the compensation tube C, both of which are contained in a cylinder filled with water (Fig. 140).

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* According to A. Wohl (*Ber.*, **1904**, 433) the results are not quite accurate when obtained in this way because the molar volume does not always equal the theoretical value of 22.41 l. Nernst, in his book, *Theoretical Chemistry*, gives the following molar volumes:

For 1 g-mol. of the gas,	or referred to oxygen
H_2 = 22.43 l	H_2 = 1.0017
O_2 = 22.39 l	O_2 = 1.0000
CO = 22.39 l	CO = 1.0000
CH_4 = 22.44 l	CH_4 = 1.0020
CO_2 = 22.26 l	CO_2 = 0.9939

Taking these values into consideration, A. Wohl obtains for x CO, y CH_4, and z H_2, the following formulas:

$$x = 0.3329\ V_c - V_o + 1.3394\ V_k$$
$$y = -0.3336\ V_c + 1.0020\ V_o - 0.3340\ V_k$$
$$z = 1.0005\ V_c - 1.0017\ V_o - 0.0060\ V_k$$

F. Haber (*Thermodynamik techn. Gasreaktionen*) sees no reason for modifying the Bunsen formulas in this way, for when a combustion analysis is carried out by explosion, the volume of gas after the explosion is so poor in carbon dioxide that the partial pressure of the latter does not vary much from that of an ideal gas, and, therefore, follows Avogadro's Rule.

It is quite another matter in the case of mixtures rich in carbon dioxide, as often occur in gas-volumetric analyses. In that case the weight of carbon dioxide (or of carbonate) is computed from the volume of the gas and accurate values are obtained by using the observed molar volume of 22.26 for this gas (see p. 351).

The necessity of using the observed molar volume instead of the theoretical value has been shown by Treadwell and Christie (*Z. angew. Chem.*, **1905**, 1930) for chlorine. With other vapors (NH_3, HCl, SO_2, N_2O) also, the observed molar volume should be used.

† *Ber.*, **21** (1888), 3242.

Through the stopcocks a and b, connect B and C, by means of capillary glass tubing containing a drop of a colored solution (indigo and sulfuric acid); in order to determine the position of the solution, the capillary is provided with a millimeter graduation. The three-way cock a can be turned so that C connects with the outer air or with the capillary,

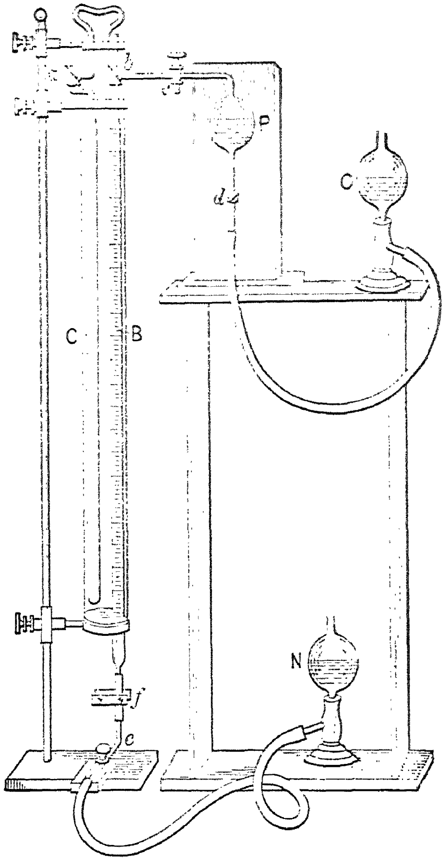

FIG. 140.

or so that the capillary is in connection with the air; it has an opening through the top of the key. The cock b has a right-angled boring like H, Fig. 131. The buret is divided into millimeters and must be calibrated with mercury before using. The apparatus is used in the same way as described under the Hempel method, p. 717.

Technical Gas Analysis

Method of Hempel

The apparatus necessary is shown in Fig. 141. It consists of a long measuring-tube ending at the top in a thick-walled capillary tube and connected at the bottom by means of rubber tubing about a meter long with the leveling-tube.

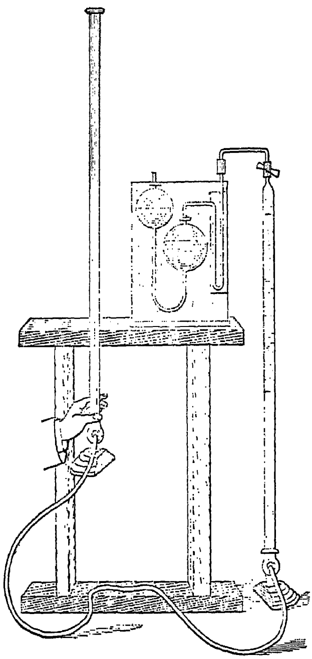

Fig. 141.

The gas is confined over water which has been saturated with the gas to be examined, and the absorption is effected in Hempel's absorption pipets such as are shown in Figs. 142, 143, 144, and 145. Fig. 142 represents a *simple* pipet for liquid absorbents, and Fig. 143 shows a *compound* absorption pipet. It is used for solutions which undergo change on exposure to the air, *e.g.*, an alkaline solution of pyrogallol, or an ammoniacal cuprous chloride solution. The liquid in the two right-hand bulbs serves to protect the solutions on the left. Fig. 144 shows the pipet used for fuming sulfuric acid. The small bulb is filled by the glass-blower with glass beads, which serve to give to the sulfuric acid the largest possible surface, so that the absorption is effected much more readily. Fig. 145 is a pipet used for solid absorbents, such as phosphorus, etc. In order to fill it with phosphorus, hold the pipet upside down, fill the cylindrical part with distilled water, and introduce small sticks of colorless phosphorus. After filling the pipet, insert the rubber stopper, place the apparatus right side up, pour water into the bulb, and remove any air-bubbles in the cylindrical part of the pipet by blowing through the bulb until the water flows out from the top of the left-hand capillary; then close by means of rubber tubing and a pinchcock.

Analysis of Illuminating-gas

First, prepare the confining liquid by conducting the gas through distilled water in a wash-bottle for several minutes with constant shaking.

Completely fill the gas-buret with this liquid and then close the upper rubber tubing with a pinchcock. To fill the buret with gas, connect the receiver with the buret by a piece of rubber tubing through which

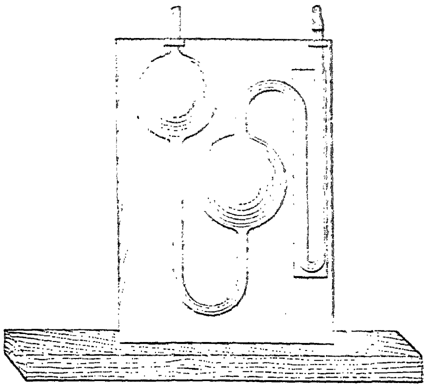

FIG. 142.

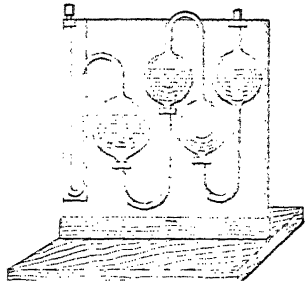

FIG. 143.

the gas has been flowing for 2 or 3 minutes, lower the leveling-tube, open the pinchcock, and allow a little more than 100 ml of the gas to flow into the buret. Now close the upper cock, raise the leveling-tube, until the lower meniscus of the confining liquid is exactly at the

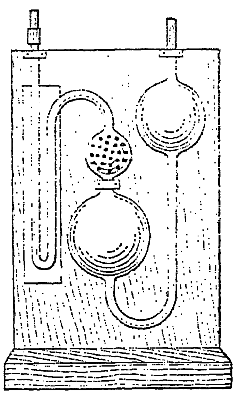

FIG. 144.

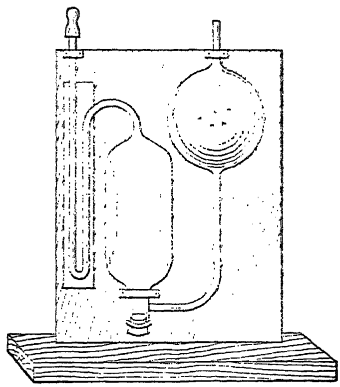

FIG. 145.

100-ml mark, and then close the rubber between the leveling-tube and the buret with a pinchcock placed near the buret, allow the apparatus to stand until the water no longer rises in the buret; this requires 2–3 minutes. When the water is stationary, carefully open the lower pinchcock (for there is excess pressure in the buret) which causes the

water-level to sink. When the 100-ml mark is again reached, close this cock, and open the upper pinchcock an instant to allow the excess of gas to escape and then immediately close. To make sure that the buret contains exactly 100 ml of the gas, open the lower pinchcock, and after bringing the water in the leveling-tube to the same height as in the buret, take the reading; the lowest point of the meniscus should coincide exactly with the 100-ml mark of the buret. Finally close the lower pinchcock.

1. Determination of Carbon Dioxide

Connect the buret with a pipet containing caustic potash solution by means of a capillary filled with water, as shown in Fig. 141, raise the leveling-tube, open first the lower pinchcock and then the upper one,* and drive the gas over into the pipet. The confining liquid should now fill the entire capillary. Close the upper pinchcock and shake the pipet and its contents for 3 minutes.† Return the gas to the buret taking care that none of the alkali enters with it.

Bring the liquid in the leveling-tube to the same level as that in the buret; close the lower pinchcock, and after the water has completely drained from the sides of the tube, read the volume of the unabsorbed gas.

2. Determination of the Heavy Hydrocarbons, or Illuminants, C_nH_{2n}

Connect the buret by a dry, empty capillary with sulfuric acid pipet (Fig. 144) and pass the gas back and forth 4 times, taking care that no water enters the pipet and that the sulfuric acid does not reach the rubber connection.

Before the experiment mark the position of the sulfuric acid upon the milk-glass plate back of the pipet and at the end of the experiment the acid must come to the same mark. The gas in the buret is now contaminated with acid vapors which are removed by passing it into the potash pipet, afterwards returning it to the buret.

3. Determination of Oxygen

This can be effected by shaking the gas in the compound pipet with alkaline pyrogallol solution, but far preferably by means of phosphorus.

* In the figure this pinchcock is lacking.

† The absorption takes place more rapidly with one of Hempel's new pipets, which is similar to the one shown in Fig. 144, except that the right-hand bulb is replaced by a movable leveling-bulb, as in Fig. 131. The latter is filled with mercury, upon which the liquid absorbent floats. For the absorption of CO_2, it is necessary to pass the gas back and forth only once.

In the latter case, drive the gas over into the phosphorus pipet and allow it to remain there until the white vapors disappear; this usually requires but 3–4 minutes (cf. p. 703). If no white vapors can be detected, this shows conclusively that the absorption of the heavy hydrocarbons was incomplete (cf. p. 704). In such a case, the gas must be again treated with sulfuric acid and afterwards with phosphorus. If no white fumes are then formed, no oxygen is present, a condition which practically never occurs, for in the determination of the hydrocarbons a little air containing oxygen always reaches the gas from the small capillary.

4. Determination of Carbon Monoxide

Shake the gas 3 minutes with an old solution of ammoniacal cuprous chloride and then the same length of time with a fresh solution. (See pp. 707, 720.)

5. Determination of Hydrogen and Methane

After the absorption of the carbon monoxide place the residual gas in the hydrochloric acid pipet and wash the buret with hydrochloric acid to remove traces of alkali, and then fill with distilled water.

Transfer 15–16 ml of the gas in the hydrochloric acid pipet to the buret, and, after reading its volume, drive it over into an explosion pipet containing mercury (Fig. 137). Accurately measure 100 ml of air (containing 20.9 ml of oxygen) in the buret and add to the contents of the explosion pipet. Then close the pipet by a pinchcock, mix the contents of the pipet by shaking, lower the leveling-tube so that the gas is placed under reduced pressure, and close the glass stopcock of the pipet. Connect the platinum wires, which are fused in the upper part of the bulb, with the poles of a small induction coil so that sparks pass between the platinum points within the pipet. The explosion at once occurs with a flash without breaking the pipet. Return the gas to the buret. Objection has been raised to reading the volume of the gas and then determining the amount of carbon dioxide formed, as a measure of the amount of methane burned, because the gas in the buret is confined over water which absorbs appreciable quantities of carbon dioxide. It has been found, however, that the error caused by absorption of CO_2 by the water is so slight, during the short time of waiting, that it is best to determine the CO_2 with caustic potash after the explosion, as Hempel also recommended. (See p. 728.) Finally, determine the amount of unused oxygen by means of absorption with phosphorus. If the excess of oxygen is subtracted from the total volume

added (20.9 ml), the volume of oxygen, V_O, required for the combustion is known (V_O), and V_C is the contraction due to combustion and absorption of the CO_2, we have two equations from which the amount of hydrogen and methane can be computed.

If x is the volume of the hydrogen, and y the volume of the methane we have

$$(1)\quad V_C = \tfrac{3}{2}\,x + 3\,y \qquad (2)\quad V_O = \tfrac{1}{2}\,x + 2\,y$$

and

$$x = \tfrac{4}{3}\,V_C - 2\,V_O \qquad y = V_O - \tfrac{1}{3}\,V_C$$

The values thus obtained are referred to the total gas residue, and in this way the amount of hydrogen and methane present in the illuminating gas can be determined.

Great accuracy is naturally not to be expected by such an analysis, but the procedure is very satisfactory for an approximate estimation. Better results are obtained by the

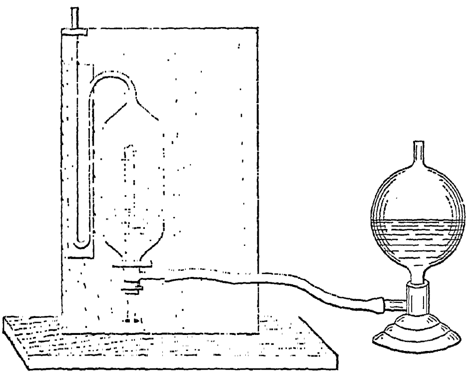

FIG. 146.

(*b*) *Method of Winkler-Dennis*

In this method, the entire gas residue is transferred to a Hempel pipet containing mercury and connected with a leveling-bulb (Fig. 146). Through the rubber stopper at the bottom two steel needles are inserted (knitting needles), the longer of which is enveloped throughout its whole length by a glass tube, and the upper end is connected, at about three-quarters the height of the cylindrical part of the pipet, with a thin platinum spiral.

Connect the pipet with a Hempel buret containing 100 ml of oxygen*

* The oxygen used for experiments in gas analysis can be prepared in the laboratory by heating potassium chlorate in a small retort, which is prepared by blowing a bulb (of about 20-ml capacity) at the end of a narrow piece of glass tubing; after introducing about 5 g of potassium chlorate, the tubing is bent to a right angle close to the bulb. Connect the end of the tube with a short piece of rubber tubing and heat the bulb over a free flame. As soon as oxygen begins to come off freely (lighting a glowing splinter) connect the rubber tubing from the retort with a Drehschmidt absorption pipet which contains a little caustic potash solution and is filled with mercury (cf. Fig. 131, p. 687). Do not at once fill the

over water, produce a lower pressure in the oxygen buret by lowering the leveling-tube and then closing the rubber tubing with a screw-cock; after this place the leveling-tube in a high position. Now connect the bottom ends of the two needles of the pipet with the wires of a small storage battery of such a strength that the platinum spiral is heated to dull redness. By lowering the leveling-bulb, reduce the pressure in the pipet slightly, and by opening the two upper screw-cocks between the pipet and the oxygen buret and gradually opening the lower screw-cock on the buret, conduct a very slow stream of oxygen into the pipet. Since a large excess of the gas residue is present at the start, the combustion takes place quietly; explosions never occur. During the combustion the platinum spiral begins to glow more brightly; to prevent its melting, place a variable resistance* in the circuit to regulate the strength of current, and the glowing of the platinum.

As soon as all the oxygen is in the pipet, allow the spiral to glow 2–3 minutes longer, then stop the electric current and allow the gas to remain in the pipet for 15 minutes so that it will assume the room temperature. Then transfer to a Hempel buret and measure its volume. Determine the carbon dioxide in the usual manner.

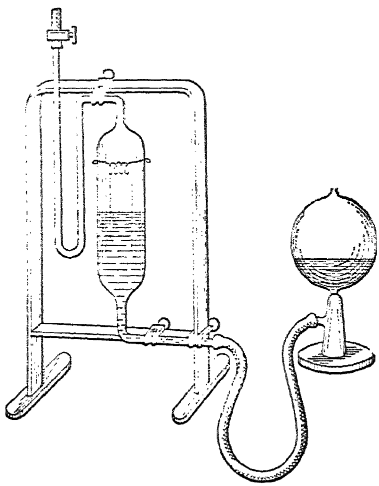

FIG. 147.

Remark. — By this method it is possible to burn pure acetylene without any explosion. The oxygen, however, must not be conducted, as above, into the acetylene because in that case the combustion of the acetylene will be incomplete and considerable carbon will deposit. First introduce oxygen into the combustion pipet, bring the platinum wire to glowing, and then introduce the acetylene; the combustion takes place smoothly without deposition of any carbon.

The Winkler-Dennis pipet is open to the objection that the rubber stopper eventu-

---

pipet but allow the gas to pass through the cock M into the air. After about a minute, one can assume that the air from the retort and rubber tubing has been entirely replaced by oxygen. Lower the leveling-bulb K of the pipet, open the cock, s, and turn the cock M 90° so that the pipet fills with oxygen. When the filling is accomplished, close M and remove the retort. By shaking the pipet any carbon dioxide formed by the burning of dust, etc., is absorbed.

* The resistance mentioned on p. 188 is suitable to use here.

ally leaks; for this reason the author prefers the form of apparatus devised by his assistant, M. Bretschger, as shown in Fig. 147.

Instead of burning the gas residue according to the Winkler-Dennis method, it may be conducted over glowing cupric oxide.*

Orsat's Apparatus

For the analysis of flue gases, Orsat has constructed the apparatus shown in Fig. 148. It consists of the 100-ml measuring-tube B surrounded by a cylinder containing water, and connected on the one hand with 3 Orsat tubes by means of the cocks I, II, III, and on the other hand with the outer air through the stopcock h. The Orsat tube III contains caustic potash solution, II alkaline pyrogallol solution, and I ammoniacal cuprous chloride solution.

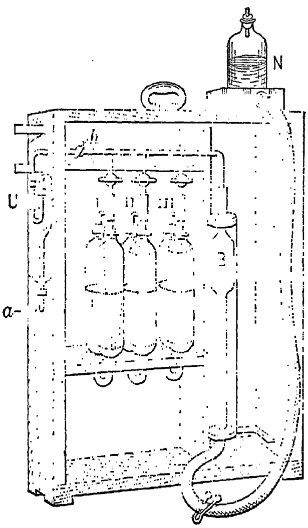

FIG. 148.

Manipulation. — By raising the leveling-bottle N and opening the stopcock h, fill the measuring-tube B with water. As soon as the water is above the mark in the widened part of the measuring-tube, close the rubber tubing between the leveling-bottle and the measuring-tube by a pinchcock. Connect a with the source of the gas, draw it into the measuring-tube by lowering the leveling-bottle and opening the pinchcock. The U-tube on the outside of the apparatus is filled with glass wool and serves as a filter; any smoke being removed from the gas to be examined. The sample thus collected is naturally contaminated with the air from the rubber tubing, the U-tube, and the capillary, which must be removed. The cock h serves for this purpose and is provided with a T-boring. Turn the cock so that the buret communicates with the outer air through a small tube (not shown in the illustration) and expel the gas by raising the bottle N. Repeat this process of filling and emptying 3 times, and use the fourth filling of the tube B for the analysis. Bring the gas in the buret to the zero-mark, and place it under atmospheric pressure by quickly opening and then closing h. After this drive over the gas into the potash-bulb and

* Jäger, *J. Gasbeleuchtung*, **1898**, 764; G. v. Knorre, *Chem. Ztg.*, **1909**, 717.

back again to the measuring-tube several times, until there is no further absorption: after this again read the volume of the gas. In the same way pass the gas successively into the pyrogallol and the cuprous chloride tubes, thus obtaining the volumes of CO_2, O_2, and CO in the gas.

Bunte's Apparatus

This apparatus, shown in Fig. 149 differs from those previously described, inasmuch as the absorption takes place in the measuring-vessel itself, whereas in the other cases the absorption takes place in the pipets.

The Bunte buret has a capacity of 110–115 ml between *a* and *b*; *a* is a three-way cock, while *b* is bored only once.

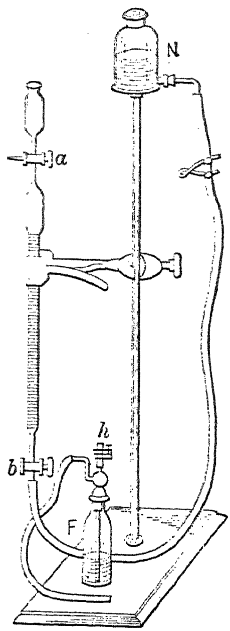

FIG. 149.

Manipulation. — Connect the buret with the leveling-bottle *N*, as shown in the illustration, open *a* and *b*, and allow the water to run up to the mark in the funnel above *a*. Connect the key of the stopcock *a* with the source of the gas, lower *N*, turn *a* to the proper position, and draw the gas into the buret. After 101–103 ml of the gas have entered the buret, close *a* and *b*, raise *N*, and by opening *b* compress the gas in the buret until the confining liquid has exactly reached the zero-mark. Now cautiously open the cock *a*, when some of the gas in the buret will escape through the water in the funnel. The gas in the buret is now under a pressure equal to that of the atmosphere plus the pressure from the column of water in the funnel, and all subsequent measurements are taken under the same conditions.

Absorptions. — In order to introduce the different absorbents into the buret connect its lower end by means of the rubber tubing *h* with the bottle *F* containing a little water and with the water blown up into the rubber tubing. Open the cock *b* and the screw-cock *h*. Allow the water in the buret to run out until it exactly reaches the cock *b*, which is then closed. Place the absorbent in a small dish, introduce the lower tip of the buret into the liquid, and open the cock *b*. Inasmuch as the gas in the buret is under less than atmospheric pressure, the absorbent is sucked up into the buret. Now close the cock *b*, grasp the buret above *a* and below *b* (in order not to warm the gas), and shake its con-

tents well; again dip the tip of the buret into the absorbent in the dish and draw up a little more of the absorbent into the buret. Repeat this process until no more of the absorbent is sucked up into the buret. It would now be incorrect to read the volume of the unabsorbed gas, for it is under a pressure quite different from that at the beginning of the analysis; namely, the atmospheric pressure less the pressure of the column of liquid remaining in the buret with the cock *b* open. Furthermore the vapor tension of the liquid in the buret is different from that of the water originally present. In order to obtain the original conditions, connect the buret with the bottle *F*, which now only contains enough water to fill the rubber tubing and the glass tube, and drain off the absorbent from the buret into the bottle until the upper level of the liquid reaches the cock *b*.* Then dip the end of the buret into a dish containing water, which rises into the buret on opening *b*. Close the latter and allow water to run into the buret from the funnel until the original pressure is established, when the volume of the gas is once more read. The difference gives at once the per cent of absorbed gas.

By means of this excellent method the carbon dioxide can be removed by caustic potash, heavy hydrocarbons by bromine water, oxygen by alkaline pyrogallol solution, and carbon monoxide by cuprous chloride.

Analysis of Gases which are Absorbed Considerably by Water

Under this heading belong N_2O, SO_2, H_2S, Cl_2, SiF_4, HF, NH_3, etc.

1. Nitrous Oxide, N_2O. Mol. Wt. 44.02

Density = 1.5297† (air = 1). Weight of 1 l = 1.9766 g
Molar volume = 22.26 l. Critical temperature = +36° C

This gas is best prepared according to the method of Victor Meyer,‡ by allowing sodium nitrite to act upon a concentrated solution of a salt of hydroxylamine:

$$NH_2OH{\cdot}HCl + NaNO_2 = NaCl + 2\,H_2O + N_2O$$

Procedure. — Add a concentrated, aqueous solution of sodium nitrite drop by drop from a separatory funnel, with constant cooling, to a concentrated solution of hydroxylamine hydrochloride in a small evolution flask; in this way the gas evolved is pure and escapes in a regular stream. It is not advisable to proceed in the opposite way, namely,

* The absorbent is now by no means exhausted, so that it can be returned to the proper bottle, and used for several more determinations.

† Lord Rayleigh, *Proc. Roy. Soc.*, **74**, 181 (1904).

‡ *Ann. Chem. Pharm.*, **157**, 141.

to add the hydroxylamine solution to a concentrated nitrite solution, for then the decomposition is likely to take place with explosive violence; it is still less advisable to add one of the reagents in the solid form. In a very dilute condition the solutions scarcely act upon one another.

Nitrous oxide is never pure when it is prepared by heating ammonium nitrate; it is always contaminated with nitrogen and nitric oxide, but the oxide may be removed by washing the gas with a solution of ferrous sulfate.

According to L. Pollak the solubility of nitrous oxide between 0° and 22° C is expressed by the formula $\beta = 1.13719 - 0.042265 \cdot t + 0.000610 \cdot t^2$, but according to Bunsen its solubility is greater, being expressed by the formula $\beta = 1.305 - 0.04536 \cdot t + 0.000684 \cdot t^2$.

The gas is absorbed to a much greater extent by alcohol than by water. According to Pollak, the absorption coefficient for alcohol is, $\beta = 3.2280 - 0.04915 \cdot t + 0.00023 \cdot t^2$, but according to Bunsen it is somewhat greater: $\beta = 4.1781 - 0.06982 \cdot t + 0.000609 \cdot t^2$.

The determination of nitrous oxide can be effected with accuracy by combustion, and this may be carried out in two different ways:

1. According to Bunsen, by exploding with hydrogen, or according to v. Knorre, by means of the Drehschmidt capillary. The contraction produced is equal to the original volume of the nitrous oxide:

$$\underset{1\text{ vol.}}{N_2O} \qquad \underset{1\text{ vol.}}{} \qquad \underset{0\text{ vol.}}{H_2O} \qquad \underset{1\text{ vol.}}{}$$

2. According to Pollak, by combustion with pure carbon monoxide, either by explosion or with the help of the Drehschmidt capillary; the volume of the CO_2 formed, which is measured, is equal to the volume of the nitrous oxide:

$$\underset{1\text{ vol.}}{N_2O} + \underset{1\text{ vol.}}{CO} = \underset{1\text{ vol.}}{CO_2} + \underset{1\text{ vol.}}{N_2}$$

There is no contraction in this case.

2. Nitric Oxide, NO. Mol. Wt. 30.01

Density = 1.0366* (air = 1). Weight of 1 l = 1.3402 g
Molar volume = 22.39 l. Critical temperature = −94° C

Preparation of Nitric Oxide

Pure nitric oxide can be prepared (*a*) according to L. Winkler,† by adding 50 per cent sulfuric acid from a dropping funnel to a dilute

* Computed from observations of Gray (1905), Guye and Davila (1906).

† *Ber.*, **34**, 1408 (1901).

solution of 1 part potassium iodide and 2 parts potassium nitrite in
solution of 1 part potassium iodide and 2 parts potassium nitrite in a fractionating flask. At the laboratory temperature, the following reaction takes place: $2\,HNO_2 + 2\,HI = 2\,H_2O + I_2 + 2\,NO$, and by washing the gas with potassium hydroxide solution, a pure gas is obtained.

(*b*) According to Emich,* by shaking a nitrate solution with concentrated sulfuric acid and mercury in a nitrometer: $2\,KNO_3 + 6\,Hg + 5\,H_2SO_4 = 2\,KHSO_4 + 3\,Hg_2SO_4 + 4\,H_2O + 2\,NO$. This method is suitable for preparing small quantities of nitric oxide. A somewhat less pure gas, but one suitable for many purposes, can be prepared by

(*c*) the method of Deventer.† Place a concentrated solution of potassium ferrocyanide and somewhat less than an equivalent weight of sodium nitrite in a flask and introduce 80 per cent acetic acid from a dropping funnel. A steady stream of gas is produced

$$2\,K_4Fe(CN)_6 + 2\,KNO_2 + 4\,HC_2H_3O_2 = 4\,KC_2H_3O_2 + 2\,K_3Fe(CN)_6 + 2\,H_2O + 2\,NO$$

which L. Moser‡ found to contain 90–97 per cent of NO and 3–10 per cent N_2.

ABSORPTION COEFFICIENTS OF NITRIC OXIDE FOR WATER§

Temperature	β	Temperature	β
0°	0.07381	30°	0.04004
5°	0.06461	35°	0.03734
10°	0.05709	40°	0.03507
15°	0.05147	45°	0.03311
20°	0.04706	50°	0.03152
25°	0.04323	55°	0.03040

Although nitric oxide is only slightly soluble in water, its determination will be discussed at this place because this gas frequently occurs with nitrous oxide, and must therefore be determined at the same time.

Nitric oxide may be determined by absorption with a concentrated solution of ferrous sulfate or an acid solution of potassium permanganate, likewise, according to E. Divers,‖ by an alkaline solution of sodium sulfite (40 g Na_2SO_3 + 4 g KOH in 200 ml H_2O) with the

* *Monatsh.*, **13**, 73 (1892).
† *Ber.*, **26**, 589 (1893).
‡ *Z. anal. Chem.*, **1911**, 406.
§ L. W. Winkler, *Ber.*, **34**, 1414 (1901).
‖ *J. Science Coll. Imp. University;* Tokyo, **11**, 11 (1893).

formation of $Na_2N_2O_2SO_3$.* It can be determined accurately according to Baudisch,† as follows: Introduce a measured volume of the gas into an absorption pipet filled with mercury and containing a moist stick of solid potassium hydroxide and add, from a buret, a measured volume of air. The NO gas is immediately oxidized to N_2O_3, which is absorbed by the potassium hydroxide: $4\,NO + O_2 + 4\,KOH = 2\,H_2O + 4\,KNO_2$. Since 5 volumes of gas disappear for each 4 volumes of NO originally present, it is evident that the contraction, V_C, is $\frac{5}{4}$ as large as the original volume of NO and NO = 0.8 V_C.

According to v. Knorre and Arndt,‡ NO can also be determined by combustion. Mix the gas with hydrogen and pass the mixture very slowly through a Drehschmidt capillary (p. 687) heated to bright redness. Under these conditions the nitric oxide is reduced to nitrogen.

$$2\,NO + 2\,H_2 = 2\,H_2O + N_2, \text{ and the volume of } NO = \tfrac{2}{3}\,V_C$$

If the mixture is passed too rapidly through the capillary tube containing the glowing platinum or if the catalyst is not hot enough, appreciable quantities of ammonia are formed and the results are inaccurate.

It is not possible to carry out the reaction in an explosion pipet: with pure NO and H_2 there is no explosion and if considerable NO_2 is present the reaction is not quantitative although a very violent explosion may occur.

Combustion of Nitric Oxide and Carbon Monoxide in a Drehschmidt Capillary

According to Henry a mixture of carbon monoxide and nitric oxide is not explosive. On the other hand, according to Pollak, by conducting a mixture of these gases through a Drehschmidt platinum capillary heated to bright redness, the combustion is quantitative if at the same time the carbon dioxide formed is removed by means of caustic potash;§ otherwise the oxidation is not quantitative. According to the equation

$$\underset{2\text{ vols.}}{2\,NO} + \underset{2\text{ vols.}}{2\,CO} = \underset{0\text{ vol.}}{2\,CO_2} + \underset{1\text{ vol.}}{N_2}$$

the contraction produced is equal to $\frac{3}{2}$ the volume of the nitric oxide.

* Nitric oxide is only partially absorbed by an alkaline solution of pyrogallol, forming alkali nitrite, N_2O, and N_2. C. Oppenheim, *Ber.*, **36**, 1744 (1903).

† *Ber.*, **46**, 3232 (1913).

‡ *Ber.*, **21**, 2136 (1889).

§ Cover the mercury in the Drehschmidt tube with a concentrated caustic potash solution, by which means the CO_2 is absorbed immediately after its formation.

Remark. — If considerable nitrous oxide is present at the same bustion in the Drehschmidt capillary takes place quantitatively with of the carbon dioxide. In this case the the xide:

Analysis of a Mixture of Nitrous and Nitric Oxides

I. *Combustion with Hydrogen*

Mix the gas with an excess of hydrogen and pass it through the Drehschmidt platinum capillary heated to bright redness as described above. If the volume of the $N_2O = x$ and that of the $NO = y$, we have: (1) $x + y = V$. (2) $x + \frac{3}{2} y = V_C$ (contraction), from which can be calculated: $x = 3\,V - 2\,V_C$, $y = 2\,(V_C - V)$.

II. *Combustion with Carbon Monoxide*

To the gas mixture add an excess of carbon monoxide, pass through the red-hot platinum capillary, and determine first the contraction, V_C, and then the carbon dioxide, V_K. If x is the volume of N_2O, y the volume of NO, then $x + y = V_K$ and $\frac{1}{2} y = V_C$, from which it follows: $x = V_K - 2\,V_C$ and $y = 2\,V_C$.

Determination of Nitrous Oxide, Nitric Oxide, and Nitrogen in the Presence of One Another

I. *By Combustion with Hydrogen in a Drehschmidt Capillary*

After noting the contraction formed by the combustion with hydrogen, add an excess of oxygen to the gas residue and burn the mixture in the Drehschmidt capillary; two-thirds of the contraction which now takes place is equal to the amount of unused hydrogen in the first oxidation. If this quantity is deducted from the amount of hydrogen originally added, the difference, V_H, represents the amount of hydrogen necessary.

We have now:

$$\begin{array}{llll} & N_2O & NO & N_2 \\ 1. & x + & y + z & = V \\ 2. & x + & \frac{3}{2} y & = V_C \\ 3. & x + & y & = V_H \end{array}$$

from which we can compute

$$x = 3\,V_H - 2\,V_C$$

$$- V_H)$$

II. *By Combustion with Carbon Monoxide in the Drehschmidt Capillary*

In this case, using the same notation, $x + y + z = V$, $0.5\,y = V_C$, and $x + y = V_K$ (volume of carbon dioxide). From this it follows: $x = V_K - 2\,V_C$, $y = 2\,V_C$, and $z = V - V_K$.

Determination of Nitrous Oxide, Nitric Oxide, and Nitrogen in the Presence of Carbon Dioxide

The accurate determination of nitrous oxide in the presence of carbon dioxide offers great difficulties. It is not possible to determine the former by combustion with hydrogen in the Drehschmidt capillary, because when the carbon dioxide is present it takes part to some extent in the combustion, $CO_2 + H_2 = H_2O + CO$, and the previous absorption of the carbon dioxide by means of a large quantity of caustic potash is equally unsatisfactory, because considerable nitrous oxide will be absorbed by the reagent. The best way to effect this determination consists in absorbing the carbon dioxide by solid, moist potassium hydroxide contained in an absorption pipet filled with mercury. The difference in volume before and after the absorption gives the volume of CO_2. Transfer the residual gas to the mercury pipet, add a measured volume of air and absorb the NO as described on p. 735. In the residue determine N_2O according to p. 733, and the N_2 by difference.

3. Nitrogen, N_2. Mol. Wt. 28.02

Density = 0.96727 (air = 1). Weight of 1 l = 1.2505 g
Molar volume = 22.41 l. Critical temperature = $-149°$ C

Pure nitrogen is best prepared by heating a concentrated solution of potassium nitrate and ammonium chloride, present in amounts proportional to their molecular weights, and then conducting the escaping gas over glowing copper to reduce traces of nitric oxide.

Nitrogen is but slightly soluble in water.

ABSORPTION COEFFICIENTS OF NITROGEN FOR WATER*

Temperatu		Temperature	
0	0.02348	30	0.01340
5	0.02081	35	0.01254
10	0.01857	40	0.01183
15	0.01682	45	0.01129
20	0.01542	50	0.01087
25	0.01432	55	0.01051

* L. Winkler, *Ber.*, **24**, 3606 (1891).

Nitrogen cannot be determined by any of the ordinary methods of gas analysis. It is usually estimated by determining all the other constituents present in a mixture and subtracting the sum of the percentages found from 100.

Technical preparations of nitrogen, prepared from the air, always consist of nitrogen and small amounts of rarer elements. According to Cavendish these latter may be obtained by adding oxygen and allowing a strong electric spark to pass through the mixture. In this way the nitrogen is completely oxidized to nitric acid, which can be removed by means of caustic potash solution. Then, by absorbing out the oxygen, the rarer gases are obtained. A still better process is that of Hempel, in which the nitrogen is absorbed by passing the gas over a glowing mixture of 1 g magnesium, 5 g freshly burnt lime, and 0.25 g sodium. The rare gases are not absorbed by this treatment.

According to Bunsen, there is no combustion of nitrogen when detonating gas explodes in the presence of air, provided not more than 30 volumes of combustible gas are present for each 100 volumes of noncombustible gas. There is no oxidation of nitrogen during a combustion of a gas mixture which is passed through a Drehschmidt platinum capillary.

Analysis of Gases by Titration of the Absorbed Constituents

If a mixture of gases contains several constituents, of which two are removed by the same absorbent, and one of these can be determined by titration, it is a matter of no difficulty to determine the amount of each. The diminution in volume after treatment with the absorbent represents the amount of the two constituents, the titration value represents the amount of one of them, and the difference shows the amount of the other. Such problems can be solved in a variety of ways, and only a few examples will be mentioned.

1. Chlorine, Cl_2. Mol. Wt. = 70.92

Density = 2.488 (air = 1).* Weight of 1 l = 3.216 g
Molar volume = 22.04 l. Critical temperature = +146° C

Determination of Carbon Dioxide in Electrolytic Chlorine†

The apparatus shown in Fig. 150 is suitable for this purpose.

* Leduc, *Compt. rend.*, **116**, 968 (1893); Treadwell and Christie, *Z. angew. Chem.*, **47**, 446 (1905).

† Treadwell and Christie, *Z. angew. Chem.*, **47**, 1930 (1905).

Fill the absolutely dry eudiometer, *B* (the capacity of which between the two stopcocks is accurately known, and for convenience may be 100 ml), through the lower cock, after drying the gas by passing it through a long calcium chloride tube.* After 5–10 minutes it is safe to assume that the air has been completely replaced by the gas. Now close the lower three-way cock and then the upper one. Note the temperature and barometric pressure.

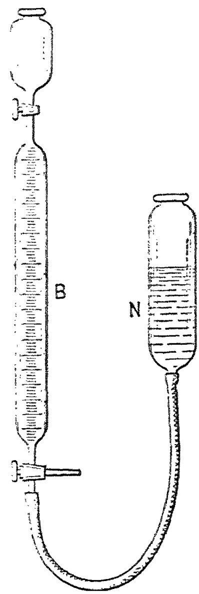

Fig. 150.

Connect the tip of the buret with the reservoir *N* by rubber tubing. Turn the three-way cock so that the reservoir communicates with the outer air, and then thoroughly wash the lower tip of the buret and the stopcock, and close the latter. Prepare a solution of potassium arsenite by dissolving 4.95 g As_2O_3 in dilute potassium hydroxide, adding dilute sulfuric acid until the solution is neutral to phenolphthalein, and then diluting to 1 l.† Place 100 ml of this solution in *N* and expel any air in the rubber tubing by pinching it with the thumb and finger. By raising *N* and opening the stopcock, cause a little of the arsenite solution to flow into the buret which is inclined from side to side in such a way that the walls are thoroughly wet with the arsenite solution. The chlorine is slowly absorbed, as is evident from the fact that the solution slowly rises in the buret. As soon as there is no further absorption, close the lower stopcock and make the solution in the buret flow back and forth several times, by inverting the buret and then turning it back again. After 1–2 minutes all the chlorine will have been absorbed. Then in order to absorb all the carbon dioxide present, lower the tube *N*, pour 10 ml of potassium hydroxide solution (1 : 1) in the funnel, and carefully introduce it into the buret. Again close the stopcock and run the alkali solution back and forth in the buret.

After bringing the liquid in the buret and in the leveling-tube to the same height, take the reading. By deducting this from the original volume of the gas, the volume of the chlorine plus that of the carbon dioxide is obtained. To determine the chlorine, empty the contents

* If the buret and gas are not perfectly dry, some chlorine will be absorbed by the water. This will not affect the gas reading, but will be harmful in the subsequent titration.

† An ordinary solution of arsenite prepared with sodium bicarbonate cannot be used here.

of the buret and of the leveling-tube into a large Erlenmeyer flask and turn the stopcock to the position shown in the drawing so that the liquid in the rubber tubing can flow out. Remove the tubing from the buret and rinse it out with distilled water which is also allowed to run into N. Now add the contents of the buret and rinse the buret itself with distilled water.

To the contents of the Erlenmeyer flask add 2 drops of phenolphthalein solution, hydrochloric acid until the red color just disappears, 60 ml of 3.5 per cent sodium bicarbonate solution, and a little starch solution. Titrate the excess of the arsenious acid with 0.1 N iodine solution.

Determine the ratio of the arsenite solution to the iodine in the same way as in the above titration. Place 100 ml of arsenite solution in an Erlenmeyer flask, add 10 ml of caustic-potash solution, 2 drops of phenolphthalein, hydrochloric acid to decolorization, and then 60 ml of sodium bicarbonate solution. Dilute to the same volume as that of the original experiment and titrate with iodine. If n milliliters were used in the analysis and n_1 milliliters are required in the direct titration of the sodium arsenite solution then $n' - n$ multiplied by 1.102* gives the number of milliliters of chlorine gas at 0° C and 760 mm pressure. In other words,

$$V_0' = (n' - n) \times 1.102$$

However, as the original gas was measured at the temperature t° C and under the pressure B millimeters, it follows, according to p. 677, that

$$V_0' = \frac{V' \cdot B \cdot 273}{760 \cdot (273 + t)}$$

from which can be computed

$$V' = \frac{V_0' \cdot 760\ (273 + t)}{B \cdot 273}$$

If V is the original volume of the gas used and R that of the residual gas in the buret, then

$$\begin{array}{rcl} Cl_2 + CO_2 + \text{residue} &=& V \\ \text{residue} &=& R \\ \hline Cl_2 + CO_2 &=& V - R \\ - Cl_2 &=& V' \\ \hline CO_2 &=& V - (R + V') \end{array}$$

* This value is derived from the fact that the density of chlorine is 2.488 at 20°,

$$\frac{70.92}{0.001293 \times 2.488} = 22{,}040$$

Therefore, 35.46 g of chlorine at 0° and 760 mm occupy a volume of 11,020 ml.

and in percentage

$$x = \frac{[illegible] \div [illegible] \cdot 100}{} = \text{per cent}$$

Schloetter* has described another method for the examination of electrolytic chlorine gas. The chlorine is absorbed by means of hydrazine sulfate, whereby 2 volumes of chlorine set free 1 volume of nitrogen. The carbon dioxide is then absorbed by means of caustic soda solution.

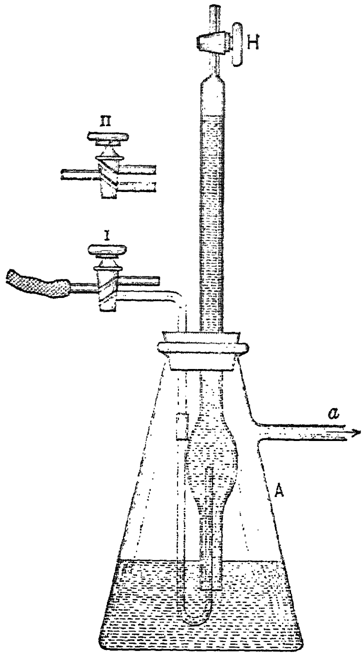

FIG. 151.

P. Ferchland† determines the chlorine by absorption with mercury in the residual gas after the CO_2 has been absorbed with caustic potash. This last method, according to the experiments of Busvold,‡ gives good results; it is to be recommended especially for the analysis of chlorine gas from the Deacon process.

Examination of the Unabsorbed Gas Residue. — Usually the residual gas is too small in amount (as in the above case) to examine quantitatively, so that for this part of the analysis a larger sample of the gas should be taken. The apparatus shown in Fig. 151§ has been used for this purpose with good results. The thick-walled filter-bottle *A* has a capacity of about 1.5 l. It contains about 500 ml of strong caustic potash solution and the absorption tube with stopcock *H* is fastened airtight within it.

Manipulation. — First fill the absorption tube with the caustic potash solution by suction through *H*, finally closing *H*. Then turn the pat-

* *Z. angew. Chem.*, **1904**, 301.

† *Z. Elektrochem.*, **13**, 114.

‡ *Inaug. Dissert.*, Zürich, 1909, also P. Philosophoff, *Chem. Ztg.*, **1907**, 959.

§ This apparatus has been used often by the author in the study of electrolytic chlorine gas and was described first in this text-book. Since then a similar apparatus has been recommended by Thiele and Deckert, *Z. angew. Chem.*, **20**, 437 (1907).

ent cock to the position *II*, and by suction through the left side-arm, fill the glass tube with the caustic alkali solution up to the cock. Turn the cock to the position *I*, connect the left side-arm, by means of a short piece of rubber tubing and a long piece of glass tubing, with the source of the gas, and aspirate several liters of gas through this tube. As soon as it is safe to assume that all of the air has been driven out from the tubing turn the cock to the position *II*, connect the aspirator at *a* with the flask *A* in which a slight vacuum is produced, whereby the gas begins to collect in the absorption tube. Chlorine and carbon dioxide are completely absorbed, while the residual gas collects in the upper part of the absorption tube. Allow the gas to enter the tube until 50–70 ml of the gas residue are obtained; then close the cock *I*, remove the aspirator, drive the gas over into a Hempel's gas-buret, and analyze according to the methods already described.

Sixty and nine-tenths milliliters of the gas residue from electrolytic chlorine containing 99.0 per cent Cl_2 and 0.6 per cent CO_2, gave:

$$\left.\begin{array}{lr} \text{Oxygen} & = 40.7 \\ \text{Carbon monoxide} & = 2.6 \\ \text{Nitrogen} & = \underline{17.6} \\ & 60.9 \end{array}\right\} \quad \text{and in per cent} \quad \left\{\begin{array}{lr} O_2 & = 66.9 \\ CO & = 4.3 \\ N_2 & = \underline{28.8} \\ & 100.0 \end{array}\right.$$

At the carbon electrode (the anode) not only chlorine but also a small amount of oxygen is liberated. The oxygen attacks the carbon of the electrode, forming carbon monoxide, the greater part of which in turn combines with the chlorine, forming phosgene gas, $COCl_2$, but this is decomposed by water with the formation of CO_2 and HCl:

$$COCl_2 + H_2O = CO_2 + 2\,HCl$$

This accounts for the presence of the CO_2 and CO in chlorine which has been prepared electrolytically.

2. Hydrochloric Acid HCl. Mol. Wt. 36.47

Density = 1.2686 (air = 1).* Weight of 1 l = 1.6400 g
Molar volume = 22.24 l. Critical temperature = +52° C

Hydrochloric acid is determined in gas mixtures by absorption in standardized alkali hydroxide solution.

3. Sulfur Dioxide. Mol. Wt. 64.07

Density = 2.2639 (air = 1).* Weight of 1 l = 2.9267 g
Molar volume = 21.89 l. Critical temperature = +155° C

For the determination of sulfur dioxide from pyrite burners, F. Reich recommends that the gas should be drawn by means of an aspirator through a measured amount of 0.1 N iodine solution, colored blue with starch, until the latter is decolorized. The amount of the gas is equal to the quantity of water which has flowed from the aspirator + the volume of the absorbed SO_2.

For example, 10 ml of 0.1 N iodine solution were decolorized after V milliliters of water had flowed from the aspirator; the gas was at $t°$ C and 760 mm pressure. Since in the absorption of the SO_2 by the iodine the following reaction takes place

$$SO_2 + H_2O + I_2 = 2\,HI + SO_3$$

it is evident that the amount of SO_2 absorbed, measured dry at 0° and 760 mm pressure, was 10.95 ml, for 1 ml 0.1 N iodine solution corresponds to 1.095 ml SO_2.

It follows, then, that the volume of gas taken for the analysis equals

$$\frac{V \cdot (B - w) \cdot 273}{760 \cdot (273 + t)} + 10.95 \text{ ml} = V_1$$

and the original gas contained $\frac{1095}{V_1}$ per cent SO_2.

Other examples of gas analyses in which the absorbed constituent is estimated by titration are found in the determination of the hydrogen sulfide in gas mixtures (see below) and in the determination of carbonic acid in the atmosphere by the method of Pettenkofer (cf. p. 534).

4. Hydrogen Sulfide, H_2S. Mol. Wt. 34.08

Density = 1.1895 (air = 1).† Weight of 1 l = 1.5378 g
Molar volume = 22.16 l. Critical temperature = 100° C

Determination of Hydrogen Sulfide in Gas Mixtures

Hydrogen sulfide, when present in the gases escaping from mineral springs, can be estimated as follows:

Lower a large funnel of 2–3 l capacity, into the spring and hold it in place by means of a wooden frame B weighted with stones, s (Fig. 152). Remove the rubber tubing d from the flask a, open the stop-

* Leduc, *Compt. rend.*, **117**, 219 (1893).

† *Ibid.*, **125**, 571 (1897).

cock h, and fill the funnel T by means of suction, with water up to stopper, and then close h. As soon as the water in the funnel been replaced by the ascending bubbles of gas, connect the one side with the stopcock tube h and on the other side the aspirator A by means of a long rubber tubing. Start suction by opening H and continue aspirating with h open until the water in the funnel T again reaches the stopper, then close h. Allow the funnel to fill with gas again, and eventually remove this through a by means of suction. Repeat this operation twice more. In this way the neck of the funnel, the glass tube h, the rubber tubing d, and the flask a, all have the air originally present in them replaced by gas from the spring; a few drops of water are carried along mechanically into a.

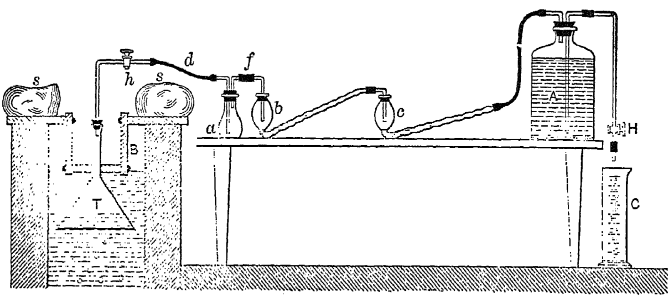

FIG. 152.

Introduce 10 ml of $0.01\,N$ iodine solution into the ten-bulb tube b and place 10 ml of 0.01 thiosulfate solution in the tube c. Quickly connect the flask a with b by means of a short piece of rubber tubing f, and connect c with the aspirator A by means of a longer piece of tubing. Meanwhile the funnel T is again filling with gas. Place a measuring cylinder, C, under the outlet tube of the bottle A, open H, and cautiously turn the stopcock h. Allow the gas to bubble slowly through b until the iodine solution becomes light yellow, but is not decolorized. Now close H and after about 2 minutes h also. Pour the contents of c into b, add starch and titrate the excess of the thiosulfate with $0.01\,N$ iodine solution (cf. p. 630). The number of milliliters, n, of iodine required for the titration, represents the amount of iodine which reacted originally with the hydrogen sulfide. The position of the water in the graduate (V milliliters), the temperature of the room $t°$, and the barometer reading B are all noted; w is the tension of aqueous vapor at the temperature $t°$.

In computing the amount of hydrogen sulfide in the gases escaping

from the spring, it is to be remembered that the volume of gas which is taken for the analysis is equal to the amount of water which has flowed into c plus the volume of hydrogen sulfide which has been absorbed by the iodine in b during the experiment. However, inasmuch as the amount of the iodine is small in comparison with the total amount of gas taken for analysis, it may be neglected here. Furthermore, it is necessary to call attention to the fact that the volume of gas escaping from the spring is at a different temperature from that of the analysis; all the volumes, therefore, should be reduced to correspond to the temperature at the spring. The amount of hydrogen sulfide present per liter in the spring gases at the temperature $t°$ and the barometric pressure B is

$$308.4 \frac{n(}{V(} \qquad = \text{ml} \qquad \text{liter}^*$$

5. Determination of Ethylene, according to Haber

The principle of this method was discussed on p. 701. The determination is effected in the Bunte buret (cf. p. 731, Fig. 149).

First, determine the contents of the lower portion of the buret from the lowest scale division to the cock by weighing the water drawn from between these points, after allowing the buret to drain. Then introduce about 90 ml of the gas to be examined into the buret and take the thermometer and barometer readings. Then, exactly as described on p. 731, draw down the liquid by suction to the stopcock,† pour a little bromine water into a small evaporating-dish, allow about 10 ml of the liquid to rise into the buret, and, in order to wash the bromine water from the tip into the buret, add 2 or 3 ml of water.

Thoroughly wet the walls of the buret with the bromine water, by suitably turning and inclining the tube; in this way the ethylene is quickly absorbed. To determine the excess of bromine, allow a strong solution of potassium iodide to rise into the buret and vigorously shake. Run out the liquid into an Erlenmeyer flask, carefully wash the buret with water, and titrate the deposited iodine with 0.1 N sodium thiosulfate solution. Determine the titer of the bromine water by pouring a little into a porcelain dish, pipeting off 10 ml of it, allowing this amount to run into a solution of potassium iodide, and titrating the liberated iodine with 0.1 N sodium thiosulfate solution.

* In this formula the temperature of the spring does not come into consideration because the gas is at the laboratory temperature when measured. The volume V is expressed in liters.

† After about 1 minute liquid will collect above the stopcock, owing to the drainage of the liquid from the sides of the buret; this is removed before adding the bromine.

The method of calculating the results will be illustrated best by means of an example.

Example. — A gas consisting of 90 volumes of air and 10 volumes of ethylene was used for the analysis. Taken for analysis, 91.2 ml of the mixture. Temperature, 18.3°. Barometer reading, 725 mm. Tension of aqueous vapor at 18.3° = 15.6 mm mercury.

Volume of the ungraduated portion of the buret...............	6.10 ml
Reading of the bromine water in the graduated part	10.00 ml
Bromine water used.................................	16.10 ml

Titer of the bromine water:

Ten milliliters of the bromine water correspond to 12.0 ml 0.1 *N* sodium thiosulfate solution, so that 16.10 ml of bromine water are equivalent to 19.32 ml of 0.1 *N* sodium thiosulfate.

We have now:

16.1 ml bromine water....................	= 19.32 ml 0.1 *N* solution
16.1 ml bromine water + ethylene...........	= 12.23 ml 0.1 *N* solution
The ethylene corresponds to...............	7.09 ml 0.1 *N* solution

Since the absorption of the ethylene by the bromine water takes place according to the equation

$$C_2H_4 + Br_2 = C_2H_4Br_2$$

it follows that

2 Br = 2 I = 20,000 ml 0.1 *N* sodium thiosulfate solution = 22,270* ml ethylene gas. Since 1 ml 0.1 *N* sodium thiosulfate corresponds to 1.114 ml C_2H_4, the 7.09 ml of 0.1 *N* solution used represent 7.09 × 1.110 = 7.94 ml C_2H_4 at 0° C and 760 mm pressure, or 9.10 ml C_2H_4 at 18.3° C and 725 mm measured, moist.

$$\left.\begin{array}{r} C_2H_4 = 9.1 \\ \text{Air} = 82.1 \end{array}\right\} \text{ and in per cent } \left\{\begin{array}{l} C_2H_4 = 10.0 \text{ per cent} \\ \text{Air} = 90.0 \text{ per cent} \end{array}\right.$$

$$\overline{91.2} \qquad\qquad \overline{100.0 \text{ per cent}}$$

This method is especially suited for the determination of ethylene present with benzene in illuminating-gas. In one sample the sum of the two gases can be determined by absorption with fuming sulfuric acid or bromine water, and in a second sample the ethylene as described above.

Remark. — Instead of using bromine water, which changes its strength so rapidly, it is better to use a tenth-normal solution of potassium bromate; on acidifying an equivalent quantity of bromine is obtained if bromide is also present.

The experiment is carried out as follows: Exactly as described above, introduce 90 ml of the gas into the Bunte buret, withdraw the water till the lower cock is reached, place some potassium bromate in a small porcelain dish, draw up about 10 ml of it into the buret, and

* Cf. p. 697.

determine the volume. Then, after wiping off the lower capillary, add an excess of concentrated potassium bromide solution and finally introduce an excess of dilute hydrochloric acid. After shaking 8 minutes, all the ethylene will be brominated. At the end of this time, allow 10 per cent potassium iodide solution to enter the buret, shake and empty into an Erlenmeyer flask. Titrate the iodine thus liberated with 0.1 *N* sodium thiosulfate solution. The calculation is carried out as before.

6. Determination of Ethylene in the Presence of Acetylene

In one sample determine the sum of the ethylene and acetylene by absorption in fuming sulfuric acid and determine the ethylene by the bromate-bromide absorption method, just described. In the cold, acetylene is not absorbed by dilute bromine water, and this method is suitable for determining ethylene in the presence of small quantities of acetylene. If considerable acetylene is present some acetylene is likely to be absorbed.

The acetylene, however, may be removed by means of a 20 per cent solution of mercuric cyanide in 2 *N* sodium hydroxide. Use 10 ml of the solution for each 50 ml of the gas mixture. Have the absorbent over the mercury in an absorption pipet. After the removal of the acetylene, ethylene can be removed by the following reagent: Dissolve 20 g $Hg(NO_3)_2$ in 100 ml of 2 *N* HNO_3 and saturate the solution with $NaNO_3$. Use 5 ml of the absorbent over mercury for the absorption of ethylene. After this benzene can be absorbed in fuming sulfuric acid and then CO, CH_4 and H_2 in the usual way.

Gas-volumetric Methods

If as a result of a chemical reaction a gas is evolved, from the volume of which the weight of the original substance can be computed.

Examples of this sort of an analysis were given under the determination of CO_2 in carbonates (pp. 350, 352, 356, 357), the carbon contents of iron and steel (pp. 369 and 371), and the NO_3 in nitrates (p. 403).

At this place a few more important determinations of the same nature will be described.

1. Determination of Ammonia in Ammonium Salts

The following method, first proposed by Knop* and later modified by P. Wagner,† depends upon the fact that ammonia is oxidized by sodium hypobromite with evolution of nitrogen:

$$2\,NH_3 + 3\,NaOBr = 3\,H_2O + 3\,NaBr + N_2$$

* *Chem. Centralbl.*, 1860, p. 243.

† *Z. anal. Chem.*, XIII (1874), p. 383; XV (1876), p. 250.

The nitrogen is collected in an azotometer and measured.

If the amount of the ammonia is calculated from the volume of the nitrogen, too low results will be obtained, and this fact was formerly explained by the assumption that a part of the nitrogen was absorbed as such by the alkaline bromite solution. This is not true. At ordinary temperatures not all the ammonia is oxidized according to the above equation to water and nitrogen, but a small quantity of ammonium hypobromite is formed; for this reason too little nitrogen is obtained in the azotometer. If, on the other hand, the decomposition takes place at 100°, the reaction goes quantitatively according to the equation. It is inconvenient to work at such a high temperature, so that it is more practical to make a correction to the volume of nitrogen obtained at ordinary temperatures.

Reagents and apparatus required:

1. An *ammonium chloride solution*, obtained by dissolving 8.356 g of the pure sublimed salt in water and diluting to 500 ml; 10 ml of this solution evolve at 0° C and 760 mm pressure 35 ml of nitrogen.

2. *Sodium hypobromite solution.* Dissolve 100 g of sodium hydroxide in water, dilute to 1250 ml and after cooling the flask in cold water, add 25 ml of bromine, vigorously shake the contents of the flask, and again cool.

This solution must be preserved in a stoppered bottle and protected from the action of light.

3. An azotometer. Instead of Wagner's* azotometer Lunge's Universal Apparatus (Fig. 70, *b*, p. 353), or any such measuring instrument may be used.

Procedure. — Place 10 ml of the standard ammonium chloride solution in the small Wagner decomposition bottle (Fig. 70, *a*, p. 353) and pour 40–50 ml of the hypobromite solution into the glass L (which is fused to the bottom of the bottle H). Then connect the bottle with the measuring-tube A,† which is entirely filled with mercury, open b, and lower the leveling-tube B. Incline the bottle H so that some of the hypobromite solution comes in contact with the solution of ammonium chloride and mix the two liquids by gentle shaking. A lively evolution of nitrogen at once takes place and the liquid becomes heated. As soon as the action ceases, allow fresh hypobromite solution to act upon the ammonium salt and repeat the process until finally all of the hypobromite is in the outer part of H. As soon as no more gas is evolved by shaking, place the decomposition bottle in water at the room temperature and after allowing it to stand 10 minutes, read the volume of the nitrogen under the conditions described on p. 354. The

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* *Loc. cit.*

† The contents of the decomposition bottle are previously cooled to the room temperature before the cock b is connected with it.

volume of nitrogen at 0° and 760 mm thus found will be smaller than the theoretical value of 35 ml, but it corresponds to the amount of ammonia contained in 10 ml of the ammonium chloride solution, *i.e.*, 0.05320 g NH_3.

Carry out several determinations and take the mean of the results obtained for the correct value.

After this, weigh out some of the ammonium salt to be analyzed, dissolve in water, and dilute so that 10 ml of the solution will contain approximately the same amount of ammonia as in the case of the standard solution. Then if, for example, from a grams of an ammonium salt, V_1 milliliters of nitrogen at 0° and 760 mm pressure were found, and V milliliters were obtained from 0.05320 g of NH_3 in the standardization, then

$$\frac{V_1 \times 5.320}{V \cdot a} = \text{per cent N}$$

Remark. — The results obtained by this method agree with those obtained by the distillation method described on p. 509. Only with substances containing thiocyanates are the results obtained too high; in this case the thiocyanate is decomposed by the alkaline hypobromite solution with evolution of nitrogen and carbon monoxide.†

Consequently, the above method affords uncertain results in the analysis of the ammonia in gas liquors.

Urea is decomposed by the alkaline hypobromite solution according to the equation:

$$CO(NH_2)_2 + 3\ NaOBr = 3\ NaBr + CO_2 + N_2 + 2\ H_2O‡$$

so that it can be determined in the same way as ammonium salts, the carbon dioxide produced by the decomposition being kept back by means of caustic soda solution.

2. Determination of Nitrous and Nitric Acids

Principle. — If a solution of a nitrite or nitrate is shaken with mercury and an excess of sulfuric acid, all the nitrogen is set free as nitric oxide:

$$2\ HNO_2 + 2\ Hg + H_2SO_4 = 2\ H_2O + Hg_2SO_4 + 2\ NO$$
$$2\ HNO_3 + 6\ Hg + 3\ H_2SO_4 = 4\ H_2O + 3\ Hg_2SO_4 + 2\ NO$$

From the volume of the nitric oxide, the weight of the nitrate or nitrite is computed.

* Lunge (Lunge-Berl, *Chem. techn. Untersuchungsmethoden*) does not standardize against the solution of ammonium chloride of known strength, but adds 2.2 per cent more ammonia to correspond to the loss of nitrogen. Then $V \times 0.001558$ = g ammonia.

† Donath and Pollak, *Z. angew. Chem.*, **1897**, 555.

‡ This reaction does not take place as completely as with ammonium salts. Lunge finds in the determination of urea in urine that the nitrogen deficit is 9 per cent. If, therefore, the volume of nitrogen after being reduced to 0° and 760 mm is multiplied by 2.952, the correct urea value is obtained.

The analysis is best performed in a Lunge nitrometer,* which is a Bunte buret in which the lower stopcock is lacking and the lower end is connected with a leveling-tube containing mercury. By raising the latter, completely fill the nitrometer (which need not be graduated) with mercury and then close the two-way cock under the funnel. Place a weighed amount of the substance dissolved in a little water in the funnel, lower the leveling-tube, and introduce the solution into the nitrometer by carefully opening the cock. Wash out the funnel 4 times with 2–3 ml of concentrated sulfuric acid. Now remove the decomposition tube from the frame, place it several times in a nearly horizontal position, and then quickly change to a vertical position. By this means the mercury becomes intimately mixed with the acid and the decomposition at once begins. Continue mixing 1–2 minutes until there seems to be no further increase in the volume of the liberated gas. Then connect the decomposition vessel by means of a short piece of rubber tubing with the gas-buret filled with mercury, transfer the nitric oxide to the latter, and read its volume after reducing it to the standard conditions by means of the gas-compensation tube. (Cf. pp. 353–355, Fig. 70, *b*.)

If in an analysis, *a* grams of a nitrate were taken and V_0 milliliters corresponds to the volume of NO at 0° and 760 mm, we have:

$$x = \frac{V_0 \times 62.01}{\quad}$$

and in per cent:

$$\frac{6201}{22391} \times \frac{v_0}{a} = 0.2769 \times \frac{V_0}{a} = \text{per cent } NO_3$$

Remark. — For the analysis of "nitrose," the author knows of no method which gives such exact results.

For the determination of nitrous acid in the presence of nitric acid by a gas-volumetric method, P. Gerlinger† treats the neutral solution of the two salts with a concentrated solution of ammonium chloride, whereby the following reaction takes place:

$$NH_4Cl + KNO_2 = 2\,H_2O + KCl + N_2$$

Half of the nitrogen evolved, therefore, comes from the nitrous acid present.

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* *Ber.*, **1890**, 440, and *Z. angew. Chem.*, **1890**, 139. See also Lunge-Berl, *Chem. techn. Untersuchungsmethoden.*

† *Z. angew. Chem.*, **1901**, 1250. Cf. J. Gaihlot, *J. Pharm. Chem.*, **1900**, 9.

Hydrogen Peroxide Methods

Hydrogen peroxide in many cases acts as an *oxidizing* agent; in other cases it has a marked *reducing* action, and by shaking with inert solids it is decomposed slowly into water and oxygen.

This anomalous behavior can be explained very easily by assuming that one of the oxygen atoms in hydrogen peroxide has one positive and one negative charge as valence bonds.

When hydrogen peroxide decomposes spontaneously on standing, a reaction which is often aided by shaking with an inert substance, such as sand, this neutral oxygen atom is lost and oxygen molecules are formed. When hydrogen peroxide acts as an *oxidizing agent*, this neutral oxygen atom is reduced to its normal negative valence of two. When hydrogen peroxide acts as a *reducing agent*, gaseous oxygen is always one of the products of the reaction. It is usually assumed that half of the evolved oxygen comes from the oxidizing agent and half from the hydrogen peroxide. Thus

$$2\ MnO_4^- + 5\ H_2O_2 + 6\ H^+ = 2\ Mn^{++} + 8\ H_2O + 5\ O_2$$

In the two following methods which involve the use of hydrogen peroxide, a large excess of the peroxide should not be used and long-continued shaking should be avoided.

(a) Standardization of Permanganate Solutions

The determination is best made according to Lunge in a gas volumeter (p. 353, Fig. 70). To obtain correct results, however, it is absolutely necessary that no excess of hydrogen peroxide be present. Consequently it is necessary to determine by means of a preliminary experiment the exact value of the permanganate solution in terms of the H_2O_2 solution used (cf. p. 570). Then place a measured amount of the latter in the outside part of the Wagner decomposition bottle (Fig. 70*a*, p. 353), and add 30 ml of 6 N sulfuric acid. After this, introduce the exact amount of hydrogen peroxide required for the decomposition of the permanganate into the inner part of the bottle and connect the bottle with the measuring-tube, which is filled with mercury, the cock *b* being removed for the time being, but it is replaced at the end of 2–3 minutes and turned to the position shown in the figure.

Then mix the two liquids, taking care to hold the decomposition flask so that its contents will not be warmed by the heat of the hand, inclining it to an angle of about 90°, and shaking for exactly 1 minute. While the oxygen is being evolved, care must be taken that the gas in the eudiometer is under reduced pressure. After the decomposition

is accomplished, place the gas under atmospheric
and by means of the compensation tube, reduce the
to what it would

manganate.

Remark. — The volume of permanganate to be taken for the experiment is determined by the size of the measuring-tube. If it has a capacity of 150 ml, 15 ml of a 0.2 N solution or 40–50 ml of a 0.1 N solution should be taken.

The hydrogen peroxide used should not be too concentrated; a 2 per cent solution is suitable. The available oxygen present in a sample of pyrolusite* can be determined by the same procedure.

(b) Determination of Cerium in Soluble Ceric Salts

If hydrogen peroxide is added to an acid solution of a soluble ceric salt, the salt is reduced with evolution of oxygen:

$$2\,Ce^{++++} + H_2O_2 = 2\,Ce^{+++} + 2\,H^+ + O_2$$

The determination is accomplished in precisely the same way as was described above in the standardization of the permanganate solution. If the volume of liberated oxygen under standard conditions is multiplied by 0.01536, the product represents the corresponding weight of CeO_2.†

Remark. — If a large excess of hydrogen peroxide is avoided in the above analysis, satisfactory results will be obtained.

Silicon Fluoride, SiF_4. Mol. Wt. = 104.06

Density = 3.605 (air = 1). Weight of 1 l = 4.660 g
Molar volume = 22.40 l

Determination of Fluorine as Silicon Fluoride (Hempel and Oettel)‡

Principle. — If a mixture of calcium fluoride and powdered quartz is treated with concentrated sulfuric acid in a glass vessel, all the fluorine will be expelled as silicon fluoride:

$$2\,CaF_2 + SiO_2 + 2\,H_2SO_4 = 2\,CaSO_4 + 2\,H_2O + SiF_4$$

and this gas can be collected and measured.

One milliliter SiF_4 at 0° and 760 mm pressure corresponds to 0.006978 g CaF_2, or 0.003395 g F_2.

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* Lunge's *Alkali Makers' Handbook.*

† Assuming that the atomic weight of Ce = 140.13.

‡ *Gasanalytische Methoden.*

Procedure. — Mix a weighed amount of the very finely powdered substance, which must not contain any other acid that can be expelled by treatment with concentrated sulfuric acid,* with 3 g of finely powdered ignited quartz, and introduce into the *dry* decomposition flask *K* (Fig. 153). Evacuate the flask somewhat by twice lowering the leveling-tube *N* with the stopcock *H* open, closing the cock and expelling the air. At the beginning of the experiment, the buret *H* should not be connected with the Orsat tube *O*. By raising the ground-glass tube *R*, cause about 30 ml of concentrated sulfuric acid to flow into the flask. This acid must have been previously heated in a porcelain crucible for some time at a temperature near the boiling point, to destroy every trace of organic matter, and allowed to cool in a desiccator over phosphorus pentoxide. Heat the acid in *K* to boiling with the stopcock *H* open and frequently shake. During the entire experiment, keep the mercury level in the tube *N* a little lower than that of the mercury in the measuring-tube *M*.†

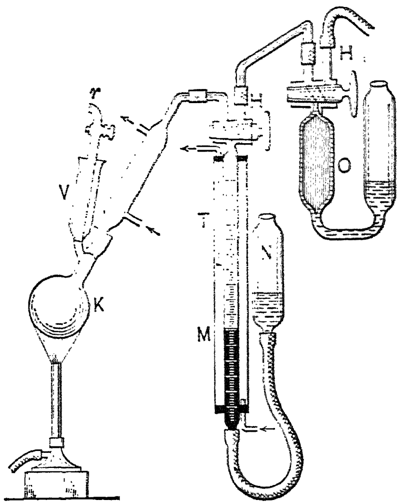

FIG. 153.

At first the sulfuric acid foams considerably, but soon ceases, which is a sure sign that the decomposition is complete. Then remove the flame, allow the sulfuric acid to cool, and expel all the gas in *K* by introducing through *V* sulfuric acid, which has been previously heated and cooled as described above. As soon as the sulfuric acid reaches the stopcock *H*, close it. After waiting 10 minutes more, place the gas under atmospheric pressure, by suitably raising *N*, and note the volume and temperature.

Now drive the gas over into the Orsat tube *O*, containing caustic potash solution (1 : 2). The silicon tetrafluoride is immediately absorbed. Return the residual gas to the tube *M*, and after waiting 15 minutes read the volume. The difference between the two readings gives the volume of silicon tetrafluoride.

* Cf. pp. 423, 424.

† To keep the inside of *N* perfectly dry, place 2–3 ml of concentrated sulfuric acid on top of the mercury.

Remarks. — A. Koch tested this method in the author's laboratory and obtained results varying from 98.97 to 102.63 per cent with pure calcium fluoride. To obtain this accuracy, however, it is necessary to carry out the decomposition under approximately atmospheric pressure. When working under a vacuum the results were always too low. Thus in one case only 85.70 per cent of the theoretical value was obtained.

During these experiments with reduced pressure, a white sublimate formed at the lower part of the condenser, which on coming in contact with the sulfuric acid that is introduced at the last, caused a strong effervescence. Since all the gas in the buret was replaced, however, we believed that the low results could be traced to the absorption of silicon fluoride by the sulfuric acid. This idea proved to be false, for a measured volume of silicon fluoride does not change when allowed to stand for 24 hours over concentrated sulfuric acid. The error, therefore, must be caused by the deposit that has condensed in the lower part of the condenser. If the work is carried out under atmospheric pressure as described above, the white deposit is never obtained.

The method can be used for the estimation of fluorine in the presence of carbonates. In this case the silicon fluoride is absorbed by means of a little water and the carbon dioxide by means of caustic potash. However, as a little of the carbon dioxide is dissolved by the water, the gas residue which has been freed from carbon dioxide is shaken with this water again, whereby this dissolved carbon dioxide is removed and can be absorbed by a further treatment with caustic potash solution. For further details, consult the original paper by Hempel and Scheffler.*

Determination of Water Vapor in Gas Mixtures

In gas analysis it is a common practice to express the results in percentages by volume. Thus if a mixture of oxygen and carbon dioxide measures V_1 milliliters under atmospheric pressure and after the carbon dioxide has been absorbed the residual gas measures V_2 milliliters under the same pressure, it is customary to assume that the original gas contained $V_1 - V_2$ milliliters of CO_2 and V_2 milliliters of oxygen. A little consideration will show that this is really an inexact assumption although it is true that the original mixture could be obtained by mixing the indicated volumes of carbon dioxide and oxygen.

When two or more gases are mixed, each occupies the total volume of the mixture. This is an apparent contradiction because two bodies cannot occupy the same space. With a gas, however, the actual volume taken up by the molecules is very small compared to the total volume occupied by the gas, and it is customary to neglect it in gas analysis. Thus at 0° and 1 mm pressure, 1 l of hydrogen gas contains only 0.16 ml of space actually occupied by hydrogen molecules. Under higher pressures, the actual volume occupied by the molecules becomes less.

In V milliliters of carbon dioxide and oxygen under atmospheric

* *Z. anorg. Chem.* [illegible]

pressure, therefore, there are present V milliliters of carbon dioxide and V milliliters of oxygen, and the pressure of the mixture is the combined pressures of the two gases. In any gas mixture, *the total pressure is the sum of the partial pressures.*

In a mixture of two gases, the percentage composition can be easily computed if the volume of the gas mixture is known under a definite pressure and temperature, and, at the same time, the partial pressure of one of the gases is known. Moreover, the ratio of the partial pressures of the gases shows the relative volumes provided the gases were measured singly under the same pressure and at the same temperature.

Applications. — 1. *Reduction of Volumes of Moist Gases to a Dry Condition at* 0° *and* 760 *mm.* If a gas is saturated with water vapor at any temperature, the partial pressure exerted by the water is known. Water evaporates until the vapor pressure of the liquid water is exactly balanced by the gas pressure exerted by the evaporated water and this is independent of whether other gases are present or not. The table on pp. 774–776 gives the vapor pressures of water at various temperatures. If a gas saturated with water vapor occupies a volume V_t at $t°$ and P millimeters pressure (of liquid mercury) and w is the tension of aqueous vapor at this temperature, then the volume occupied by the dry gas at 0° and 760 mm pressure would be $V_0 = V_t \dfrac{(P - w)\,273}{760\,(273 + t)}$.

2. *Calculation of the Moisture in the Air at Normal Pressure* (760 *mm*) *and Temperature* $t°$.

What is the percentage of moisture (by volume) of air saturated with moisture at 0°, 25°, and 35°? According to the table: $w_0 = 4.6$ mm; $w_{25} = 23.5$ mm; and $w_{35} = 41.8$ mm. By dividing each of these values by 760 and multiplying by 100, we find the percentage of moisture to be 0.61 per cent at 0°, 3.09 per cent at 25°, and 5.50 per cent at 35°.

If the gas is not saturated with moisture, the relation of the dry gas to the moist one can be computed if the degree of saturation, or *humidity*, is known. The humidity of the gas expresses the amount of moisture as a percentage of the amount that the gas contains when saturated with moisture. Thus if the humidity is 50 per cent, the gas could take up just as much more water at the prevailing temperature. If the humidity is r, then if the given gas were measured dry at 760 mm and at the same temperature, its volume would be $\dfrac{V(P - r \cdot}{760}$ and if the water exists as gas at 760 mm pressure and the same temperature, its volume is $\dfrac{V \cdot r \cdot w}{760}$

3. *Calculation of the Weight of Water-vapor in a Given Volume of Air*, at $t°$ and P millimeters pressure, which is saturated with moisture.

If 1 ml of water exists as a gas at 0° and 760 mm pressure, it ought to weigh 0.000801 g as an ideal gas. At $t°$ and P millimeters pressure, it should weigh

$$\frac{0.000801 \times P \times 273}{760 \times (273 + t)} \text{ g}$$

If the gas is not saturated with water vapor, but the degree of saturation (the humidity) is known, then the following formula gives the weight of water-vapor present in the volume v_t of the gas,

$$\frac{0.00801 \cdot r \cdot w \cdot v_t \cdot 273}{760\ (273 + t)} \text{ g}$$

Or, if the weight of vapor present in a given gas volume is known, then from the last equation the humidity, r, of gas may be computed:

$$r = \frac{g \cdot 760\ (273 + t)}{0.000801 \cdot w \cdot v_t \cdot 273}$$

Density Tables

One of the easiest methods for determining the percentage composition of a solution containing only one dissolved substance is to determine the density of the solution. This, however, is not a reliable method of analysis because the density of a solution is never strictly proportional to the quantity of dissolved substance, and if a density curve is plotted for all possible concentrations, it will sometimes be found that there are, at certain parts of the curve, two different concentrations that have the same density.

Instead of determining the *density* of a solution, or weight of the unit volume, it is often customary to determine the weight of the solution as compared to the weight of the same volume of another liquid. Water is commonly taken as the basis of comparison, and since 1 ml of water at 4° weighs 1 g, the specific gravity when referred to water at this temperature is the same as the density, when this is defined as the weight in grams of 1 ml of water.

Unfortunately, however, usage has not been uniform in the choice of temperature at which the specific gravities have been taken, and the comparison is often made with water at the same temperature.

The extensive application of hydrometers as measuring instruments in the collection of revenues in commerce and for buying and selling certain liquids has led the U. S. Bureau of Standards to define the vari-

ous scales in terms of fundamental units. Some of the tables in this book are taken from this source. About 15 years previously the Manufacturing Chemists' Association of the United States published tables, which have been copied in quite a number of text-books, in which the specific gravities were taken at 60° Fahrenheit and referred to water at the same temperature.

Whenever a specific gravity value is given, the *modulus* should also be stated. Thus a specific gravity at $\frac{60°}{60°}$ F means that the comparison was made at 60° F with water at the same temperature, and $\frac{15°}{4°}$ C means that the comparison was made at 15° C with water at 4° C.

The confusion, however, does not end here. Just as certain civilized countries, particularly England and the United States, have been slow to adopt the metric system, so the people of most countries have held tenaciously to other scales for determining relative masses of equal volumes of liquids. Thus the English Twaddell scale and the various French Baumé scales are still in constant use. Throughout the text of this book, the metric system has been used for the sake of simplicity, and, as far as the analytical chemist is concerned, density tables are, on the whole, more satisfactory than specific gravity tables. Data will be given, however, showing how these tables can be translated into other units.

TABLE I. — DENSITY OF WATER AT DIFFERENT TEMPERATURES*

t	Density	*t*	Density	*t*	Density
0°	0.999867	14°	0.999271	28°	0.996258
1	9926	15	9126	29	0.995969
2	9968	16	8969	30	5672
3	9992	17	8801	31	5366
4	1.000000	18	8621	32	5052
5	0.999992	19	8430	33	0.994728
6	9968	20	8229	34	4397
7	9929	21	8017	35	4058
8	9876	22	0.997795	36	0.993711
9	9808	23	7563	37	3356
10	9727	24	7321	38	0.992993
11	9632	25	7069	39	2622
12	9524	26	0.996808	40	0.992244
13	9404	27	6538		

* P. Chappuis.

TABLE 2. — WEIGHT OF 1 GALLON OF WATER

Based on the work of Chappuis and of Thiesen. Water is assumed to be weighed in dry air at the same temperature up to 40°. Above 40°, the temperature of the air is assumed to be 20°. The calculations were on the assumption that 1 l = 61.023 in. The water is distilled water containing a normal quantity of "heavy water."

Temperature		Weight in Grams	Weight in Pounds
°C	°F		
0	32	3780.5	8.3346
4	39.2	3781.1	8.3359
10	50	3780.1	8.3338
15	59	3777.9	8.3289
15.56	60	3777.6	8.3282
20	68	3774.6	8.3216
25	77	3770.3	8.3121
30	86	3765.1	8.3006
40	104	3752.2	8.2723
50	122	3736.2	8.2369
60	140	3717.9	8.1966
70	158	3697.4	8.1514
80	176	3674.8	8.1015
90	194	3650.3	8.0474
100	212	3623.9	7.9894

TABLE 3. — WEIGHT OF 1 CU. FT. OF WATER

Temperature		Weight in Grams	Weight in Pounds
°C	°F		
0	32	28,280	62.347
4	39.2	28,284	62.357
10	50	28,277	62.335
15	59	28,261	62.305
15.56	60	28,259	62.299
20	68	28,236	62.250
25	77	28,204	62.179
30	86	28,165	62.093
40	104	28,068	61.881

TABLE 4. — DEGREES BAUMÉ, POUNDS PER GALLON, AND GALLONS PER POUND CORRESPONDING TO VARIOUS SPECIFIC GRAVITIES

Specific Gravity 60°/60° F	Degrees Baumé Modulus 140	Pounds per Gallon	Gallons per Pound
0.600	103.33	4.993	0.2003
.610	99.51	5.076	.1970
.620	95.81	5.160	.1938
.630	92.22	5.243	.1907
.640	88.75	5.326	.1877
.650	85.38	5.410	.1848
.660	82.12	5.493	.1820
.670	78.96	5.577	.1793
.680	75.88	5.660	.1767
.690	72.90	5.743	.1741
.700	70.00	5.827	.1716
.710	67.18	5.910	.1692
.720	64.44	5.994	.1668
.730	61.78	6.077	.1646
.740	59.19	6.160	.1623
.750	56.67	6.244	.1602
.760	54.21	6.327	.1580
.770	51.82	6.410	.1560
.780	49.49	6.494	.1540
.790	47.22	6.577	.1520
.800	45.00	6.661	.1501
.810	42.84	6.744	.1483
.820	40.73	6.827	.1465
.830	38.68	6.911	.1447
.840	36.67	6.994	.1430
.850	34.71	7.078	.1413
.860	32.79	7.161	.1396
.870	30.92	7.244	.1380
.880	29.09	7.328	.1365
.890	27.30	7.411	.1349
.900	25.56	7.494	.1334
.910	23.85	7.578	.1320
.920	22.17	7.661	.1305
.930	20.54	7.745	.1291
.940	18.94	7.828	.1278
.950	17.37	7.911	.1264
.960	15.83	7.995	.1251
.970	14.33	8.078	.1238
.980	12.86	8.162	.1225
.990	11.41	8.245	.1213
1.000	10.00	8.328	.1201

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Based on the work of Chappuis and of Thiesen. Water is assumed to be weighed in dry air at the same temperature up to 40°. Above 40°, the temperature of the air is assumed to be 20°. The calculations were on the assumption that 1 l = 61.023 in. The water is distilled water containing a normal quantity of "heavy water."

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20	68	3774.6	8.3216
25	77	3770.3	8.3121
30	86	3765.1	8.3006
40	104	3752.2	8.2723
50	122	3736.2	8.2369
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.640	88.75	5.326	.1877
.650	85.38	5.410	.1848
.660	82.12	5.493	.1820
.670	78.96	5.577	.1793
.680	75.88	5.660	.1767
.690	72.90	5.743	.1741
.700	70.00	5.827	.1716
.710	67.18	5.910	.1692
.720	64.44	5.994	.1668
.730	61.78	6.077	.1646
.740	59.19	6.160	.1623
.750	56.67	6.244	.1602
.760	54.21	6.327	.1580
.770	51.82	6.410	.1560
.780	49.49	6.494	.1540
.790	47.22	6.577	.1520
.800	45.00	6.661	.1501
.810	42.84	6.744	.1483
.820	40.73	6.827	.1465
.830	38.68	6.911	.1447
.840	36.67	6.994	.1430
.850	34.71	7.078	.1413
.860	32.79	7.161	.1396
.870	30.92	7.244	.1380
.880	29.09	7.328	.1365
.890	27.30	7.411	.1349
.900	25.56	7.494	.1334
.910	23.85	7.578	.1320
.920	22.17	7.661	.1305
.930	20.54	7.745	.1291
.940	18.94	7.828	.1278
.950	17.37	7.911	.1264
.960	15.83	7.995	.1251
.970	14.33	8.078	.1238
.980	12.86	8.162	.1225
.990	11.41	8.245	.1213
1.000	10.00	8.328	.1201

TABLE 5. — SPECIFIC GRAVITIES, POUNDS PER GALLON, AND GALLONS PER POUND CORRESPONDING TO VARIOUS DEGREES BAUMÉ

Degrees Baumé (Modulus 140)	Specific Gravity 60°/60° F	Pounds per Gallon	Gallons per Pound	Degrees Baumé (Modulus 140)	Specific Gravity 60°/60° F	Pounds per Gallon	Gallons per Pound
10.0	1.0000	8.328	0.1201	55.0	0.7568	6.300	0.1587
11.0	.9929	8.269	.1209	56.0	.7527	6.266	.1596
12.0	.9859	8.211	.1218	57.0	.7487	6.233	.1604
13.0	.9790	8.153	.1227	58.0	.7447	6.199	.1613
14.0	.9722	8.096	.1235	59.0	.7407	6.166	.1622
15.0	.9655	8.041	.1244	60.0	.7368	6.134	.1630
16.0	.9589	7.986	.1252	61.0	.7330	6.102	.1639
17.0	.9524	7.931	.1261	62.0	.7292	6.070	.1647
18.0	.9459	7.877	.1270	63.0	.7254	6.038	.1656
19.0	.9396	7.825	.1278	64.0	.7216	6.007	.1665
20.0	.9333	7.772	.1287	65.0	.7179	5.976	.1673
21.0	.9272	7.721	.1295	66.0	.7143	5.946	.1682
22.0	.9211	7.670	.1304	67.0	.7107	5.916	.1690
23.0	.9150	7.620	.1313	68.0	.7071	5.886	.1699
24.0	.9091	7.570	.1321	69.0	.7035	5.856	.1708
25.0	.9032	7.522	.1330	70.0	.7000	5.827	.1716
26.0	.8974	7.473	.1338	71.0	.6965	5.798	.1725
27.0	.8917	7.425	.1347	72.0	.6931	5.769	.1733
28.0	.8861	7.378	.1355	73.0	.6897	5.741	.1742
29.0	.8805	7.332	.1364	74.0	.6863	5.712	.1751
30.0	.8750	7.286	.1373	75.0	.6829	5.685	.1759
31.0	.8696	7.241	.1381	76.0	.6796	5.657	.1768
32.0	.8642	7.196	.1390	77.0	.6763	5.629	.1776
33.0	.8589	7.152	.1398	78.0	.6731	5.602	.1785
34.0	.8537	7.108	.1407	79.0	.6699	5.576	.1793
35.0	.8485	7.065	.1415	80.0	.6667	5.549	.1802
36.0	.8434	7.022	.1424	81.0	.6635	5.522	.1811
37.0	.8383	6.980	.1433	82.0	.6604	5.497	.1819
38.0	.8333	6.939	.1441	83.0	.6573	5.471	.1828
39.0	.8284	6.898	.1450	84.0	.6542	5.445	.1837
40.0	.8235	6.857	.1459	85.0	.6512	5.420	.1845
41.0	.8187	6.817	.1467	86.0	.6482	5.395	.1854
42.0	.8140	6.777	.1476	87.0	.6452	5.370	.1862
43.0	.8092	6.738	.1484	88.0	.6422	5.345	.1871
44.0	.8046	6.699	.1493	89.0	.6393	5.320	.1880
45.0	.8000	6.661	.1501	90.0	.6364	5.296	.1888
46.0	.7955	6.623	.1510	91.0	.6335	5.272	.1897
47.0	.7910	6.586	.1518	92.0	.6306	5.248	.1905
48.0	.7865	6.548	.1527	93.0	.6278	5.225	.1914
49.0	.7821	6.511	.1536	94.0	.6250	5.201	.1923
50.0	.7778	6.476	.1544	95.0	.6222	5.178	.1931
51.0	.7735	6.440	.1553	96.0	.6195	5.155	.1940
52.0	.7692	6.404	.1562	97.0	.6167	5.132	.1949
53.0	.7650	6.369	.1570	98.0	.6140	5.110	.1957
54.0	.7609	6.334	.1579	99.0	.6114	5.088	.1966
55.0	.7568	6.300	.1587	100.0	.6087	5.066	.1974

TABLE 6. — DEGREES BAUMÉ CORRESPONDING TO SPECIFIC GRAVITIES AT $\frac{60°}{60°}$ F $\left(\frac{15.056}{15.056}\text{ C}\right)$ FOR LIQUIDS HEAVIER THAN WATER

[Calculated from the formula degrees Baumé = $145 - \dfrac{145}{D\frac{60°}{60°}\text{F}}$ which defines the Baumé scale, in general use in the United States, for liquids heavier than water]

$D\frac{15.056}{15.056}C$	0	1	2	3	4	5	6	7	8	9	Diff.
1.00	0.000	0.145	0.289	0.434	0.578	0.721	0.865	1.008	1.151	1.293	143
1.01	1.436	1.578	1.719	1.861	2.002	2.143	2.283	2.424	2.564	2.704	141
1.02	2.843	2.982	3.121	3.260	3.399	3.537	3.675	3.812	3.950	4.087	138
1.03	4.223	4.360	4.496	4.632	4.768	4.903	5.038	5.174	5.308	5.443	136
1.04	5.577	5.711	5.845	5.978	6.111	6.244	6.377	6.509	6.641	6.773	133
1.05	6.905	7.036	7.167	7.298	7.429	7.559	7.689	7.819	7.949	8.078	130
1.06	8.208	8.336	8.465	8.594	8.722	8.850	8.978	9.105	9.232	9.359	128
1.07	9.486	9.613	9.739	9.865	9.991	10.116	10.242	10.367	10.492	10.616	126
1.08	10.741	10.865	10.989	11.113	11.236	11.359	11.483	11.605	11.728	11.850	124
1.09	11.972	12.094	12.216	12.338	12.459	12.580	12.701	12.821	12.942	13.062	121
1.10	13.182	13.302	13.421	13.540	13.659	13.778	13.897	14.015	14.134	14.252	119
1.11	14.370	14.487	14.604	14.721	14.838	14.955	15.072	15.188	15.304	15.420	117
1.12	15.536	15.651	15.767	15.882	15.997	16.111	16.226	16.340	16.454	16.568	115
1.13	16.682	16.795	16.908	17.021	17.134	17.247	17.359	17.471	17.583	17.695	113
1.14	17.807	17.919	18.030	18.141	18.252	18.363	18.473	18.583	18.693	18.803	111
1.15	18.913	19.023	19.132	19.241	19.350	19.459	19.568	19.676	19.784	19.892	109
1.16	20.000	20.108	20.215	20.322	20.430	20.536	20.643	20.750	20.856	20.962	107
1.17	21.068	21.174	21.280	21.385	21.491	21.596	21.701	21.806	21.910	22.014	105
1.18	22.119	22.223	22.327	22.430	22.534	22.637	22.740	22.843	22.946	23.049	103
1.19	23.151	23.254	23.356	23.458	23.560	23.661	23.763	23.864	23.965	24.066	101
1.20	24.167	24.267	24.368	24.468	24.568	24.668	24.768	24.868	24.967	25.066	100
1.21	25.165	25.264	25.363	25.462	25.560	25.658	25.755	25.855	25.952	26.050	98
1.22	26.148	26.245	26.342	26.439	26.536	26.633	26.729	26.826	26.922	27.018	97
1.23	27.114	27.210	27.305	27.401	27.496	27.591	27.686	27.781	27.876	27.970	95
1.24	28.065	28.159	28.253	28.347	28.441	28.534	28.628	28.721	28.814	28.907	94
1.25	29.000	29.093	29.185	29.278	29.370	29.462	29.554	29.646	29.738	29.829	92
1.26	29.921	30.012	30.103	30.194	30.285	30.376	30.466	30.556	30.647	30.737	91
1.27	30.827	30.917	31.006	31.096	31.185	31.275	31.364	31.453	31.542	31.630	89
1.28	31.719	31.807	31.896	31.984	32.072	32.160	32.247	32.335	32.422	32.510	88
1.29	32.597	32.684	32.771	32.858	32.944	33.031	33.117	33.204	33.290	33.376	87
1.30	33.462	33.547	33.633	33.718	33.804	33.889	33.974	34.059	34.144	34.229	85
1.31	34.313	34.397	34.482	34.566	34.650	34.734	34.818	34.901	34.985	35.068	84
1.32	35.152	35.235	35.318	35.401	35.483	35.566	35.649	35.731	35.813	35.895	83
1.33	35.977	36.059	36.141	36.223	36.304	36.386	36.467	36.548	36.629	36.710	81
1.34	36.791	36.872	36.952	37.033	37.113	37.173	37.273	37.353	37.433	37.513	80
1.35	37.593	37.672	37.751	37.831	37.910	37.989	38.068	38.147	38.225	38.304	79
1.36	38.382	38.461	38.539	38.617	38.695	38.773	38.851	38.928	39.006	39.803	78
1.37	39.161	39.238	39.315	39.392	39.469	39.546	39.622	39.609	39.775	39.851	77
1.38	39.928	40.004	40.080	40.156	40.231	40.307	40.382	40.458	40.533	40.608	76
1.39	40.683	40.758	40.833	40.908	40.983	41.057	41.132	41.206	41.280	41.355	75
1.40	41.429	41.503	41.576	41.650	41.724	41.797	41.871	41.944	42.017	42.090	74
1.41	42.163	42.236	42.309	42.381	42.454	42.527	42.599	42.671	42.743	42.815	73

TABLE 6.—DEGREES BAUMÉ CORRESPONDING TO SPECIFIC GRAVITIES AT $\frac{60°}{60°}$ FOR LIQUIDS HEAVIER THAN WATER.—*Continued*

$D\frac{15.056}{15.056}C$	0	1	2	3	4	5	6	7	8	9	Diff.
1.41	42.163	42.236	42.309	42.381	42.454	42.527	42.599	42.671	42.743	42.815	73
1.42	42.887	42.959	43.031	43.103	43.174	43.246	43.317	43.388	43.459	43.530	72
1.43	43.601	43.672	43.743	43.814	43.884	43.955	44.025	44.095	44.166	44.236	71
1.44	44.306	44.376	44.445	44.515	44.585	44.654	44.724	44.793	44.862	44.931	70
1.45	45.000	45.069	45.138	45.207	45.275	45.344	45.412	45.481	45.549	45.617	69
1.46	45.685	45.753	45.821	45.889	45.956	46.024	46.091	46.159	46.226	46.293	67
1.47	46.361	46.428	46.495	46.562	46.628	46.695	46.762	46.828	46.894	46.961	67
1.48	47.027	47.093	47.159	47.225	47.291	47.357	47.423	47.488	47.554	47.619	66
1.49	47.685	47.750	47.815	47.880	47.945	48.010	48.075	48.140	48.204	48.269	65
1.50	48.333	48.398	48.462	48.526	48.591	48.655	48.719	48.782	48.846	48.910	64
1.51	48.974	49.037	49.101	49.164	49.227	49.290	49.354	49.417	49.480	49.543	63
1.52	49.605	49.668	49.731	49.793	49.856	49.918	49.980	50.043	50.105	50.167	62
1.53	50.229	50.291	50.353	50.414	50.476	50.538	50.599	50.660	50.722	50.783	61
1.54	50.844	50.905	50.966	51.027	51.088	51.149	51.210	51.270	51.331	51.391	61
1.55	51.452	51.512	51.572	51.632	51.692	51.752	51.812	51.872	51.932	51.992	60
1.56	52.051	52.111	52.170	52.230	52.289	52.348	52.407	52.467	52.526	52.585	59
1.57	52.643	52.702	52.761	52.820	52.878	52.937	52.995	53.053	53.112	53.170	59
1.58	53.228	53.286	53.344	53.402	53.460	53.517	53.575	53.633	53.690	53.748	58
1.59	53.805	53.862	53.920	53.977	54.034	54.091	54.148	54.205	54.262	54.318	57
1.60	54.375	54.432	54.488	54.545	54.601	54.657	54.714	54.770	54.826	54.882	56
1.61	54.938	54.994	55.050	55.106	55.161	55.217	55.272	55.328	55.383	55.439	56
1.62	55.494	55.549	55.604	55.659	55.714	55.769	55.824	55.879	55.934	55.988	55
1.63	56.043	56.098	56.152	56.206	56.261	56.315	56.369	56.423	56.478	56.531	54
1.64	56.585	56.639	56.693	56.747	56.801	56.854	56.908	56.961	57.015	57.068	54
1.65	57.121	57.175	57.228	57.281	57.334	57.387	57.440	57.493	57.545	57.598	53
1.66	57.651	57.703	57.756	57.808	57.861	57.913	57.965	58.017	58.070	58.122	52
1.67	58.174	58.226	58.278	58.329	58.381	58.433	58.485	58.536	58.588	58.639	52
1.68	58.690	58.742	58.793	58.844	58.896	58.947	58.998	59.049	59.100	59.150	51
1.69	59.201	59.252	59.303	59.353	59.404	59.454	59.505	59.555	59.605	59.656	50
1.70	59.706	59.756	59.806	59.856	59.906	59.956	60.006	60.056	60.105	60.155	50
1.71	60.205	60.254	60.304	60.353	60.403	60.452	60.501	60.550	60.600	60.649	49
1.72	60.698	60.747	60.796	60.844	60.893	60.942	60.991	61.039	61.088	61.136	49
1.73	61.185	61.234	61.282	61.330	61.378	61.427	61.475	61.523	61.571	61.619	48
1.74	61.667	61.715	61.762	61.810	61.858	61.906	61.953	62.001	62.048	62.096	48
1.75	62.143	62.190	62.237	62.285	62.332	62.379	62.426	62.473	62.520	62.567	47
1.76	62.614	62.660	62.707	62.754	62.801	62.847	62.894	62.940	62.987	63.033	46
1.77	63.079	63.125	63.172	63.218	63.264	63.310	63.356	63.402	63.448	63.494	46
1.78	63.539	63.585	63.631	63.676	63.722	63.768	63.813	63.858	63.904	63.949	46
1.79	63.994	64.040	64.085	64.130	64.175	64.220	64.265	64.310	64.355	64.400	45
1.80	64.445	64.489	64.534	64.579	64.623	64.668	64.712	64.757	64.801	64.845	45
1.81	64.890	64.934	64.978	65.022	65.066	65.110	65.154	65.198	65.242	65.286	44
1.82	65.330	65.374	65.417	65.461	65.504	65.548	65.591	65.635	65.678	65.722	43
1.83	65.765	65.808	65.852	65.895	65.938	65.981	66.024	66.067	66.110	66.153	43
1.84	66.196	66.238	66.281	66.324	66.367	66.409	66.452	66.494	66.537	66.579	42
1.85	66.622										

TABLE 7.— SPECIFIC GRAVITIES AT $\frac{60°}{60°}$ F $\left(\frac{15.056}{15.056} \text{C}\right)$ CORRESPONDING TO DEGREES BAUMÉ FOR LIQUIDS HEAVIER THAN WATER

[Calculated from the formula specific gravity $\frac{60°}{60°}$ F $= \frac{145}{145 - \text{deg Baumé}}$]

Degrees Baumé	Tenths of Degrees Baumé									
	0	1	2	3	4	5	6	7	8	9
0	1.0000	1.0007	1.0014	1.0021	1.0028	1.0035	1.0042	1.0049	1.0055	1.0062
1	1.0069	1.0076	1.0083	1.0090	1.0097	1.0105	1.0112	1.0119	1.0126	1.0133
2	1.0140	1.0147	1.0154	1.0161	1.0168	1.0175	1.0183	1.0190	1.0197	1.0204
3	1.0211	1.0218	1.0226	1.0233	1.0240	1.0247	1.0255	1.0262	1.0269	1.0276
4	1.0284	1.0291	1.0298	1.0306	1.0313	1.0320	1.0328	1.0335	1.0342	1.0350
5	1.0357	1.0365	1.0372	1.0379	1.0387	1.0394	1.0402	1.0409	1.0417	1.0424
6	1.0432	1.0439	1.0447	1.0454	1.0462	1.0469	1.0477	1.0484	1.0492	1.0500
7	1.0507	1.0515	1.0522	1.0530	1.0538	1.0545	1.0553	1.0561	1.0569	1.0576
8	1.0584	1.0592	1.0599	1.0607	1.0615	1.0623	1.0630	1.0638	1.0646	1.0654
9	1.0662	1.0670	1.0677	1.0685	1.0693	1.0701	1.0709	1.0717	1.0725	1.0733
10	1.0741	1.0749	1.0757	1.0765	1.0773	1.0781	1.0789	1.0797	1.0805	1.0813
11	1.0821	1.0829	1.0837	1.0845	1.0853	1.0861	1.0870	1.0878	1.0886	1.0894
12	1.0902	1.0910	1.0919	1.0927	1.0935	1.0943	1.0952	1.0960	1.0968	1.0977
13	1.0985	1.0993	1.1002	1.1010	1.1018	1.1027	1.1035	1.1043	1.1052	1.1060
14	1.1069	1.1077	1.1086	1.1094	1.1103	1.1111	1.1120	1.1128	1.1137	1.1145
15	1.1154	1.1162	1.1171	1.1180	1.1188	1.1197	1.1206	1.1214	1.1223	1.1232
16	1.1240	1.1249	1.1258	1.1267	1.1275	1.1284	1.1293	1.1302	1.1310	1.1319
17	1.1328	1.1337	1.1346	1.1355	1.1364	1.1373	1.1381	1.1390	1.1399	1.1408
18	1.1417	1.1426	1.1435	1.1444	1.1453	1.1462	1.1472	1.1481	1.1490	1.1499
19	1.1508	1.1517	1.1526	1.1535	1.1545	1.1554	1.1563	1.1572	1.1581	1.1591
20	1.1600	1.1609	1.1619	1.1628	1.1637	1.1647	1.1656	1.1665	1.1675	1.1684
21	1.1694	1.1703	1.1712	1.1722	1.1731	1.1741	1.1750	1.1760	1.1769	1.1779
22	1.1789	1.1798	1.1808	1.1817	1.1827	1.1837	1.1846	1.1856	1.1866	1.1876
23	1.1885	1.1895	1.1905	1.1915	1.1924	1.1934	1.1944	1.1954	1.1964	1.1974
24	1.1983	1.1993	1.2003	1.2013	1.2023	1.2033	1.2043	1.2053	1.2063	1.2073
25	1.2083	1.2093	1.2104	1.2114	1.2124	1.2134	1.2144	1.2154	1.2164	1.2175
26	1.2185	1.2195	1.2205	1.2216	1.2226	1.2236	1.2247	1.2257	1.2267	1.2278
27	1.2288	1.2299	1.2309	1.2319	1.2330	1.2340	1.2351	1.2361	1.2372	1.2383
28	1.2393	1.2404	1.2414	1.2425	1.2436	1.2446	1.2457	1.2468	1.2478	1.2489
29	1.2500	1.2511	1.2522	1.2532	1.2543	1.2554	1.2565	1.2576	1.2587	1.2598
30	1.2609	1.2620	1.2631	1.2642	1.2653	1.2664	1.2675	1.2686	1.2697	1.2708
31	1.2719	1.2730	1.2742	1.2753	1.2764	1.2775	1.2787	1.2798	1.2809	1.2821
32	1.2832	1.2843	1.2855	1.2866	1.2877	1.2889	1.2900	1.2912	1.2923	1.2935
33	1.2946	1.2958	1.2970	1.2981	1.2993	1.3004	1.3016	1.3028	1.3040	1.3051
34	1.3063	1.3075	1.3087	1.3098	1.3110	1.3122	1.3134	1.3146	1.3158	1.3170
35	1.3182	1.3194	1.3206	1.3218	1.3230	1.3242	1.3254	1.3266	1.3278	1.3291
36	1.3303	1.3315	1.3327	1.3339	1.3352	1.3364	1.3376	1.3389	1.3401	1.3414
37	1.3426	1.3438	1.3451	1.3463	1.3476	1.3488	1.3501	1.3514	1.3526	1.3539
38	1.3551	1.3564	1.3577	1.3590	1.3602	1.3615	1.3628	1.3641	1.3653	1.3666
39	1.3679	1.3692	1.3705	1.3718	1.3731	1.3744	1.3757	1.3770	1.3783	1.3796
40	1.3810	1.3823	1.3836	1.3849	1.3862	1.3876	1.3889	1.3902	1.3916	1.3929
41	1.3942	1.3956	1.3969	1.3983	1.3996	1.4010	1.4023	1.4037	1.4050	1.4064
42	1.4078	1.4091	1.4105	1.4119	1.4133	1.4146	1.4160	1.4174	1.4188	1.4202
43	1.4216	1.4230	1.4244	1.4258	1.4272	1.4286	1.4300	1.4314	1.4328	1.4342
44	1.4356	1.4371	1.4385	1.4399	1.4414	1.4428	1.4442	1.4457	1.4471	1.4486
45	1.4500	1.4515	1.4529	1.4544	1.4558	1.4573	1.4588	1.4602	1.4617	1.4632
46	1.4646	1.4661	1.4676	1.4691	1.4706	1.4721	1.4736	1.4751	1.4766	1.4781
47	1.4796	1.4811	1.4826	1.4841	1.4857	1.4872	1.4887	1.4902	1.4918	1.4933
48	1.4948	1.4964	1.4979	1.4995	1.5010	1.5026	1.5041	1.5057	1.5073	1.5088
49	1.5104	1.5120	1.5136	1.5152	1.5167	1.5183	1.5199	1.5215	1.5231	1.5247
50	1.5263	1.5279	1.5295	1.5312	1.5328	1.5344	1.5360	1.5376	1.5393	1.5409
51	1.5426	1.5442	1.5458	1.5475	1.5491	1.5508	1.5525	1.5541	1.5558	1.5575
52	1.5591	1.5608	1.5625	1.5642	1.5659	1.5676	1.5693	1.5710	1.5727	1.5744
53	1.5761	1.5778	1.5795	1.5812	1.5830	1.5847	1.5864	1.5882	1.5899	1.5917
54	1.5934	1.5952	1.5969	1.5987	1.6004	1.6022	1.6040	1.6058	1.6075	1.6093
55	1.6111	1.6129	1.6147	1.6165	1.6183	1.6201	1.6219	1.6237	1.6256	1.6274
56	1.6292	1.6310	1.6329	1.6347	1.6366	1.6384	1.6403	1.6421	1.6440	1.6459
57	1.6477	1.6496	1.6515	1.6534	1.6553	1.6571	1.6590	1.6609	1.6628	1.6648
58	1.6667	1.6686	1.6705	1.6724	1.6744	1.6763	1.6782	1.6802	1.6821	1.6841
59	1.6860	1.6880	1.6900	1.6919	1.6939	1.6959	1.6979	1.6999	1.7019	1.7039
60	1.7059	1.7079	1.7099	1.7119	1.7139	1.7160	1.7180	1.7200	1.7221	1.7241
61	1.7262	1.7282	1.7303	1.7324	1.7344	1.7365	1.7386	1.7407	1.7428	1.7449
62	1.7470	1.7491	1.7512	1.7533	1.7554	1.7576	1.7597	1.7618	1.7640	1.7661
63	1.7683	1.7705	1.7726	1.7748	1.7770	1.7791	1.7813	1.7835	1.7857	1.7879
64	1.7901	1.7923	1.7946	1.7968	1.7990	1.8012	1.8035	1.8057	1.8080	1.8102
65	1.8125	1.8148	1.8170	1.8193	1.8216	1.8239	1.8262	1.8285	1.8308	1.8331
66	1.8354	1.8378	1.8401	1.8424	1.8448	1.8471	1.8495	1.8519	1.8542	1.8566
67	1.8590	1.8614	1.8638	1.8662	1.8686	1.8710	1.8734	1.8758	1.8782	1.8807
68	1.8831	1.8856	1.8880	1.8905	1.8930	1.8954	1.8979	1.9004	1.9029	1.9054
69	1.9079	1.9104	1.9129	1.9155	1.9180	1.9205	1.9231	1.9256	1.9282	1.9308
70	1.9333									

TABLE 8. — DEGREES BAUMÉ CORRESPONDING TO SPECIFIC GRAVITIES AT $\frac{60°}{60°}$ F $\left(\frac{15.056}{15.056} C\right)$ A. P. I. SCALE

[Calculated from the formula degrees Baumé = $\frac{141.5}{D\ 60°/60°\ F} - 131.5$, which defines the Baumé scale as used in the oil industry of the United States]*

$D\frac{15.056}{15.056}C$	0	1	2	3	4	5	6	7	8	9	Diff.
0.60	104.33	103.94	103.55	103.16	102.77	102.38	102.00	101.61	101.23	100.85	0.38
.61	100.47	100.09	99.71	99.33	98.96	98.58	98.21	97.84	97.46	97.09	.37
.62	96.73	96.36	95.99	95.63	95.26	94.90	94.54	94.18	93.82	93.46	.36
.63	93.10	92.75	92.39	92.04	91.69	91.33	90.98	90.63	90.29	89.94	.35
.64	89.59	89.25	88.90	88.56	88.22	87.88	87.54	87.20	86.86	86.53	.34
.65	86.19	85.86	85.52	85.19	84.86	84.53	84.20	83.87	83.55	83.22	.33
.66	82.29	82.57	82.25	81.92	81.60	81.28	80.96	80.64	80.33	80.01	.32
.67	79.69	79.38	79.07	78.75	78.44	78.13	77.82	77.51	77.20	76.89	.31
.68	76.59	76.28	75.98	75.67	75.37	75.07	74.77	74.47	74.17	73.87	.30
.69	73.57	73.28	72.98	72.68	72.39	72.10	71.80	71.51	71.22	70.93	.29
.70	70.64	70.35	70.07	69.78	69.49	69.21	68.92	68.64	68.36	68.08	.28
.71	67.80	67.52	67.24	66.96	66.68	66.40	66.13	65.85	65.58	65.30	.27
.72	65.03	64.76	64.48	64.21	63.94	63.67	63.40	63.14	62.87	62.60	.27
.73	62.34	62.07	61.81	61.54	61.28	61.02	60.76	60.49	60.23	59.97	.26
.74	59.72	59.46	59.20	58.94	58.69	58.43	58.18	57.92	57.67	57.42	.25
.75	57.17	56.92	56.66	56.41	56.17	55.92	55.67	55.42	55.18	54.93	.24
.76	54.68	54.44	54.20	53.95	53.71	53.47	53.23	52.98	52.74	52.51	.24
.77	52.27	52.03	51.79	51.55	51.32	51.08	50.85	50.61	50.38	50.14	.23
.78	49.91	49.68	49.45	49.22	48.98	48.75	48.53	48.30	48.07	47.84	.23
.79	47.61	47.39	47.16	46.94	46.71	46.49	46.26	46.04	45.82	45.60	22
.80	45.38	45.15	44.93	44.71	44.49	44.28	44.06	43.84	43.62	43.41	.22
.81	43.19	42.98	42.76	42.55	42.33	42.12	41.91	41.69	41.48	41.27	.21
.82	41.06	40.85	40.64	40.43	40.22	40.02	39.81	39.60	39.39	39.19	.21
.83	38.98	38.78	38.57	38.37	38.16	37.96	37.76	37.56	37.35	37.15	20
.84	36.95	36.75	36.55	36.35	36.15	35.96	35.76	35.56	35.36	35.17	.20
.85	34.97	34.77	34.58	34.39	34.19	34.00	33.80	33.61	33.42	33.23	.19
.86	33.03	32.84	32.65	32.46	32.27	32.08	31.89	31.71	31.52	31.33	.19
.87	31.14	30.96	30.77	30.58	30.40	30.21	30.03	29.85	29.66	29.48	.18
.88	29.30	29.11	28.93	28.75	28.57	28.39	28.21	28.03	27.85	27.67	18
.89	27.49	27.31	27.13	26.95	26.78	26.60	26.42	26.25	26.07	25.90	.18
90	25.72	25.55	25.37	25.20	25.03	24.85	24.68	24.51	24.34	24.17	.17
.91	23.99	23.82	23.65	23.48	23.31	23.14	22.98	22.81	22.64	22.47	.17
.92	22.30	22.14	21.97	21.80	21.64	21.47	21.31	21.14	20.98	20.81	.16
.93	20.65	20.49	20.32	20.16	20.00	19.84	19.68	19.51	19.35	19.19	.16
.94	19.03	18.87	18.71	18.55	18.39	18.24	18.08	17.92	17.76	17.60	.16
.95	17.45	17.29	17.13	16.98	16.82	16.67	16.51	16.36	16.20	16.05	.15
.96	15.90	15.74	15.59	15.44	15.28	15.13	14.98	14.83	14.68	14.53	.15
.97	14.38	14.23	14.08	13.93	13.78	13.63	13.48	13.33	13.18	13.04	.15
.98	12.89	12.74	12.59	12.45	12.30	12.15	12.01	11.86	11.72	11.57	.14
.99	11.43	11.29	11.14	11.00	10.85	10.71	10.57	10.43	10.28	10.14	.14
1.00	10.00										

* Circular No. 154, U. S. Bureau of Standards (1924). In 1904, when the Bureau of Standards at Washington, D. C., first took up the testing of hydrometers, careful inquiry showed that the so-called *Baumé scale for liquids lighter than water* was based on the formula

$$\text{Degrees Baumé} = \frac{140}{\text{sp. gr. } 60°/60°\text{ F}} - 130$$

In December, 1921, The American Petroleum Institute, the U. S. Bureau of Mines, and the U. S. Bureau of Standards adopted 141.5 and 131.5 in place of 140 and 130, to be used in the petroleum industry. The scale is known as the A. P. I. scale to distinguish it from the Baumé scale using 140.

TABLE 9. — SPECIFIC GRAVITIES AT $\frac{60°}{60°}$ F $\left(\frac{15.056}{15.056}\text{C}\right)$ CORRESPONDING TO DEGREES BAUMÉ, A. P. I. SCALE

[Calculated from the formula, specific gravity $\frac{60°}{60°}$ F $= \frac{141}{141 + \text{deg Bé}}$]

Degrees Baumé	Tenths of Degrees Baumé									
	0	1	2	3	4	5	6	7	8	9
10	1.0000	0.9993	0.9986	0.9979	0.9972	0.9965	0.9958	0.9951	0.9944	0.9937
11	0.9930	.9923	.9916	.9909	.9902	.9895	.9888	.9881	.9874	.9868
12	.9861	.9854	.9847	.9840	.9833	.9826	.9820	.9813	.9806	.9799
13	.9792	.9786	.9779	.9772	.9765	.9759	.9752	.9745	.9738	.9732
14	.9725	.9718	.9712	.9705	.9698	.9692	.9685	.9679	.9672	.9665
15	.9659	.9650	.9646	.9639	.9632	.9626	.9619	.9613	.9606	.9600
16	.9593	.9587	.9580	.9574	.9567	.9561	.9554	.9548	.9541	.9535
17	.9529	.9522	.9516	.9509	.9503	.9497	.9490	.9484	.9478	.9471
18	.9465	.9459	.9452	.9446	.9440	.9433	.9427	.9421	.9415	.9408
19	.9402	.9396	.9390	.9383	.9377	.9371	.9365	.9358	.9352	.9346
20	.9340	.9334	.9328	.9321	.9315	.9309	.9303	.9297	.9291	.9285
21	.9279	.9273	.9267	.9260	.9254	.9248	.9242	.9236	.9230	.9224
22	.9218	.9212	.9206	.9200	.9194	.9188	.9182	.9176	.9170	.9165
23	.9159	.9153	.9147	.9141	.9135	.9129	.9123	.9117	.9111	.9106
24	.9100	.9094	.9088	.9082	.9076	.9071	.9065	.9059	.9053	.9047
25	.9042	.9036	.9030	.9024	.9018	.9013	.9007	.9001	.8996	.8990
26	.8984	.8978	.8973	.8967	.8961	.8956	.8950	.8944	.8939	.8933
27	.8927	.8922	.8916	.8911	.8905	.8899	.8894	.8868	.8883	.8877
28	.8871	.8866	.8860	.8855	.8849	.8844	.8838	.8833	.8827	.8822
29	.8816	.8811	.8805	.8800	.8794	.8789	.8783	.8778	.8772	.8767
30	.8762	.8756	.8751	.8745	.8740	.8735	.8729	.8724	.8718	.8713
31	.8708	.8702	.8697	.8692	.8686	.8681	.8676	.8670	.8665	.8660
32	.8654	.8649	.8644	.8639	.8633	.8628	.8623	.8618	.8612	.8607
33	.8602	.8597	.8591	.8586	.8581	.8576	.8571	.8565	.8560	.8555
34	.8550	.8545	.8540	.8534	.8529	.8524	.8519	.8514	.8509	.8504
35	.8498	.8493	.8488	.8483	.8478	.8473	.8468	.8463	.8458	.8453
36	.8448	.8443	.8438	.8433	.8428	.8423	.8418	.8413	.8408	.8403
37	.8398	.8393	.8388	.8383	.8378	.8373	.8368	.8363	.8358	8353
38	.8348	.8343	.8338	.8333	.8328	.8324	.8319	.8314	.8309	.8304
39	.8229	.8294	.8289	.8285	.8280	.8275	.8270	.8265	.8260	.8256
40	.8251	.8246	.8241	.8236	.8232	.8227	.8222	.8217	.8212	.8208
41	.8203	.8198	.8193	.8189	.8184	.8179	.8174	.8170	.8165	.8160
42	.8155	.8151	.8146	.8142	.8137	.8132	.8128	.8123	.8118	.8114
43	.8109	.8104	.8100	.8095	.8090	.8086	.8081	.8076	.8072	.8067
44	.8063	.8058	.8054	.8049	.8044	.8040	.8035	.8031	.8026	.8022
45	.8017	.8012	.8008	.8003	.7999	.7994	.7990	.7985	.7981	.7976
46	.7972	.7967	.7963	.7958	.7954	.7949	.7945	.7941	.7936	.7932
47	.7927	.7923	.7918	.7914	.7909	.7905	.7901	.7896	.7892	.7887
48	.7883	.7879	.7874	.7870	.7865	.7861	.7857	.7852	.7848	.7844
49	.7839	.7835	.7831	.7826	.7822	.7818	.7813	.7809	.7805	.7800
50	.7796	.7792	.7788	.7783	.7779	.7775	.7770	.7766	.7762	.7758
51	.7753	.7749	.7745	.7741	.7736	.7732	.7728	.7724	.7720	.7715
52	.7711	.7707	.7703	.7699	.7694	.7690	.7686	.7682	.7678	.7674
53	.7669	.7665	.7661	.7657	.7653	.7649	.7645	.7640	.7636	.7632
54	.7628	.7624	.7620	.7616	.7612	.7608	.7603	.7599	.7595	.7591
55	.7587	.7583	.7579	.7575	.7571	.7567	.7563	.7559	.7555	.7551

TABLE 10. — SPECIFIC GRAVITIES AT $\frac{60°}{60°}$ F $\left(\frac{15.056}{15.056}\text{ C}\right)$ CORRESPONDING TO DEGREES BAUMÉ, A. P. I. SCALE — *Continued*

Degrees Baumé	Tenths of Degrees Baumé									
	0	1	2	3	4	5	6	7	8	9
55	0.7587	0.7583	0.7579	0.7575	0.7571	0.7567	0.7563	0.7559	0.7555	0.7551
56	.7547	.7543	.7539	.7535	.7531	.7527	.7523	.7519	.7515	.7511
57	.7507	.7503	.7499	.7495	.7491	.7487	.7483	.7479	.7475	.7471
58	.7467	.7463	.7459	.7455	.7451	.7447	.7443	.7440	.7436	.7432
59	.7428	.7424	.7420	.7416	.7412	.7408	.7405	.7401	.7397	.7393
60	.7389	.7385	.7381	.7377	.7374	.7370	.7366	.7362	.7358	.7354
61	.7351	.7347	.7343	.7339	.7335	.7332	.7328	.7324	.7320	.7316
62	.7313	.7309	.7305	.7301	.7298	.7294	.7290	.7286	.7283	.7279
63	.7275	.7271	.7268	.7264	.7260	.7256	.7253	.7249	.7245	.7242
64	.7238	.7234	.7230	.7227	.7223	.7219	.7216	.7212	.7208	.7205
65	.7201	.7197	.7194	.7190	.7186	.7183	.7179	.7175	.7172	.7168
66	.7165	.7161	.7157	.7158	.7150	.7146	.7143	.7139	.7136	.7132
67	.7128	.7125	.7121	.7117	.7114	.7111	.7107	.7103	.7100	.7096
68	.7093	.7089	.7086	.7082	.7079	.7075	.7071	.7068	.7064	.7061
69	.7057	.7054	.7050	.7047	.7043	.7040	.7036	.7033	.7029	.7026
70	.7022	.7019	.7015	.7012	.7008	.7005	.7000	.6998	.6995	.6991
71	.6988	.6984	.6981	.6977	.6974	.6970	.6967	.6964	.6960	.6957
72	.6953	.6950	.6946	.6943	.6940	.6936	.6933	.6929	.6926	.6923
73	.6919	.6916	.6913	.6909	.6906	.6902	.6899	.6896	.6892	.6889
74	.6886	.6882	.6879	.6876	.6872	.6869	.6866	.6862	.6859	.6856
75	.6852	.6849	.6846	.6842	.6839	.6836	.6832	.6829	.6826	.6823
76	.6819	.6816	.6813	.6809	.6806	.6803	.6800	.6796	.6793	.6790
77	.6787	.6783	.6780	.6777	.6774	.6770	.6767	.6764	.6761	.6757
78	.6754	.6751	.6748	.6745	.6741	.6738	.6735	.6732	.6728	.6725
79	.6722	.6719	.6716	.6713	.6709	.6706	.6703	.6700	.6697	.6693
80	,6690	.6687	.6684	.6681	.6678	.6675	.6671	.6668	.6665	.6662
81	.6659	.6656	.6653	.6649	.6646	.6643	.6640	.6637	.6634	.6631
82	.6628	.6625	.6621	.6618	.6615	.6612	.6609	.6606	.6603	.6600
83	.6597	.6594	.6591	.6588	.6584	.6581	.6578	.6575	.6572	.6569
84	.6566	.6563	.6560	.6557	.6554	.6551	.6548	.6545	.6542	.6539
85	.6536	.6533	.6530	.6527	.6524	.6521	.6518	.6515	.6512	.6509
86	.6506	.6503	.6500	.6497	.6494	.6491	.6488	.6485	.6482	.6479
87	.6476	.6473	.6470	.6467	.6464	.6461	.6458	.6455	.6452	.6449
88	.6446	.6444	.6441	.6438	.6435	.6432	.6429	.6426	.6423	.6420
89	.6417	.6414	.6411	.6409	.6406	.6403	.6400	.6397	.6394	.6391
90	.6388	.6385	.6382	.6380	.6377	.6374	.6371	.6368	.6365	.6362
91	.6360	.6357	.6354	.6351	.6348	.6345	.6342	.6340	.6337	.6334
92	.6331	.6328	.6325	.6323	.6320	.6317	.6314	.6311	.6309	.6306
93	.6303	.6300	.6297	.6294	.6292	.6289	.6286	.6283	.6281	.6278
94	.6275	.6272	.6270	.6267	.6264	.6261	.6258	.6256	.6253	.6250
95	.6247	.6244	.6241	.6239	.6233	.6233	.6231	.6228	.6225	.6223
96	.6220	.6217	.6214	.6212	.6209	.6206	.6203	.6201	.6198	.6195
97	.6193	.6190	.6187	.6184	.6182	.6179	.6176	.6174	.6171	.6168
98	.6166	.6163	.6160	.6158	.6155	.6152	.6150	.6147	.6144	.6141
94	.6139	.6136	.6134	.6131	.6128	.6126	.6123	.6120	.6118	.6112
100	.6112									

TABLE 11. — CONVERSION OF DENSITY BASIS

Prepared for use in reducing readings of a hydrometer graduated to indicate density or specific gravity at a specified standard temperature, T, referred to water at a specified temperature, T′, as unity, to the basis of another standard temperature, t, and reference temperature, t′.

The factor Δ (given in units of the sixth decimal place), multiplied by the density or sp reading, gives the correction to be applied to the reading to reduce it to the required basis.

Suppose a hydrometer indicates specific gravity at $\frac{20°}{4°}$C, and it is required to know the correction in order that it shall indicate specific gravity at $\frac{15.56}{15.56}$ C, then,

That is, if the hydrometer indicates correctly a specific gravity of 1.5760 at $\frac{20°}{4°}$, then at $\frac{15.56}{15.56}$ the reading of the instrument will be too low by 1.5760 × 0.001062 = 0.0017. A correction of 0.0017 must therefore be added to the indication of the hydrometer.

Or, if a maker using standards indicating D $\frac{15.56}{15.56}$ C wishes to graduate a hydrometer to indicate density at 20° C referred to water at 4° C $\left(D\frac{20}{4}\right)$ the readings of the standard must be corrected by use of the factor + 0.001062.

Suppose the standard reads	1.5760
The corresponding correction is 1.6 × .001062 =	+0.0017
Corrected reading	1.5777

The table is calculated for Jena 16[III] glass.

Given Basis of Density $\frac{T}{T'}$	Required Basis of Density $\frac{t}{t'}$: $D\frac{25°}{4°}$ C	$D\frac{20}{4}$	$D\frac{17.5}{4}$	$D\frac{15.56}{4}$	$D\frac{15}{4}$	$D\frac{15}{15}$	$D\frac{15.56}{15.56}$	$D\frac{17.5}{17.5}$	$D\frac{20}{20}$	$D\frac{25}{25}$
	Δ (In Units of the Sixth Decimal Place)									
$D\frac{25°}{4°}$ C	0	+ 115	+ 172	+ 217	+ 230	+1104	+1177	+1459	+1884	+2931
$D\frac{20}{4}$	− 115	0	+ 58	+ 102	+ 115	+ 989	+1062	+1345	+1769	+2816
$D\frac{17.5}{4}$	− 172	− 58	0	+ 45	+ 58	+ 932	+1005	+1287	+1711	+2758
$D\frac{15.56}{4}$	− 217	− 102	− 45	0	+ 13	+ 887	+ 960	+1242	+1667	+2713
$D\frac{15}{4}$	− 230	− 115	− 58	− 13	0	+ 874	+ 947	+1229	+1654	+2700
$D\frac{15}{15}$	−1103	− 988	− 931	− 886	− 873	0	+ 73	+ 354	+ 779	+1826
$D\frac{15.56}{15.56}$	−1176	−1061	−1004	− 960	− 947	− 73	0	+ 281	+ 706	+1752
$D\frac{17.5}{17.5}$	−1457	−1343	−1285	−1240	−1227	− 354	− 281	0	+ 424	+1471
$D\frac{20}{20}$	−1881	−1766	−1708	−1664	−1651	− 778	− 705	− 423	0	+1046
$D\frac{25}{25}$	−2923	−2808	−2751	−2707	−2694	−1821	−1748	−1468	−1044	0

TABLE 12. — DENSITY OF SOLUTIONS OF SULFURIC ACID (H_2SO_4) AT 20° C

[Calculated from Dr. J. Domke's table.[1] Adopted as the basis for standardization of hydrometers indicating per cent of sulfuric acid at 20° C.]

Per Cent H_2SO_4	$D\frac{20}{4}C$	Per Cent H_2SO_4	$D\frac{20}{4}C$	Per Cent H_2SO_4	$D\frac{20}{4}C$
0	0.99823	50	1.39505	91.0	1.81950
1	1.00506	51	1.40487	91.2	1.82045
2	1.01178	52	1.41481	91.4	1.82137
3	1.01839	53	1.42487	91.6	1.82227
4	1.02500	54	1.43503	91.8	1.82315
5	1.03168	55	1.44530	92.0	1.82401
6	1.03843	56	1.45568	92.2	1.82484
7	1.04527	57	1.46615	92.4	1.82564
8	1.05216	58	1.47673	92.6	1.82641
9	1.05909	59	1.48740	92.8	1.82717
10	1.06609	60	1.49818	93.0	1.82790
11	1.07314	61	1.50904	93.2	1.82860
12	1.08026	62	1.51999	93.4	1.82928
13	1.08744	63	1.53102	93.6	1.82993
14	1.09468	64	1.54213	93.8	1.83055
15	1.10199	65	1.55333	94.0	1.83115
16	1.10936	66	1.56460	94.2	1.83172
17	1.11679	67	1.57595	94.4	1.83226
18	1.12428	68	1.58739	94.6	1.83276
19	1.13183	69	1.59890	94.8	1.83324
20	1.13943	70	1.61048	95.0	1.83368
21	1.14709	71	1.62213	95.1	1.83389
22	1.15480	72	1.63384	95.2	1.83410
23	1.16258	73	1.64560	95.3	1.83430
24	1.17041	74	1.65738	95.4	1.83449
25	1.17830	75	1.66917	95.5	1.83469
26	1.18624	76	1.68095	95.6	1.83486
27	1.19423	77	1.69268	95.7	1.83503
28	1.20227	78	1.70433	95.8	1.83520
29	1.21036	79	1.71585	95.9	1.83534
30	1.21850	80	1.72717	96.0	1.83548
31	1.22669	81	1.73827	96.1	1.83560
32	1.23492	82	1.74904	96.2	1.83572
33	1.24320	83	1.75943	96.3	1.83584
34	1.25154	84	1.76932	86.4	1.83594
35	1.25992	85	1.77860	96.5	1.83604
36	1.26836	85.5	1.78300	96.6	1.83613
37	1.27685	86	1.78721	96.7	1.83621
38	1.28543	86.5	1.79124	96.8	1.83628
39	1.29407	87	1.79509	96.9	1.83634
40	1.30278	87.5	1.79875	97.0	1.83637
41	1.31157	88	1.80223	97.1	1.83639
42	1.32043	88.5	1.80552	97.2	1.83640
43	1.32938	89	1.80864	97.3	1.83640
44	1.33843	89.5	1.81159	97.4	1.83639
45	1.34759	90	1.81438	97.5	1.83637
46	1.35686	90.2	1.81545	97.6	1.83634
47	1.36625	90.4	1.81650	97.7	1.83629
48	1.37574	90.6	1.81753	97.8	1.83623
49	1.38533	90.8	1.81853	97.9	1.83615
50	1.39505	91.0	1.81950	98.0	1.83605

[1] *Wiss. Abh. der kaiserlichen Normal-Eichungs-Kommission*, 5, p. 131; 1900.

TABLE 13. — TEMPERATURE CORRECTIONS TO PER CENT OF SULFURIC ACID DETERMINED BY HYDROMETER (STANDARD AT 20° C)

[Calculated from the same data as the preceding table, assuming Jena 16[III] glass as the material used. The table should be used with caution, and only for approximate results when the temperature differs much from the standard temperature or from the temperature of the surrounding air]

Observed Per Cent H_2SO_4	Temperature in Degrees Centigrade											
	0	5	10	15	25	30	35	40	45	50	55	60
	Subtract from Observed Per Cent				Add to Observed Per Cent							
0					0.16	0.35	0.59	0.86	1.17	1.5	1.9	2.1
5	0.59	0.49	0.36	0.20	0.24	0.50	0.79	1.11	1.45	1.8	2.2	2.6
10	0.92	0.72	0.51	0.27	0.29	0.60	0.93	1.28	1.65	2.0	2.4	2.8
20	1.39	1.06	0.72	0.36	0.37	0.75	1.14	1.53	1.93	2.3	2.7	3.1
30	1.64	1.23	0.82	0.41	0.41	0.82	1.24	1.65	2.07	2.5	2.9	3.3
40	1.65	1.24	0.82	0.41	0.41	0.82	1.22	1.62	2.03	2.4	2.8	3.2
50	1.56	1.17	0.78	0.39	0.38	0.77	1.15	1.52	1.90	2.3	2.6	3.0
60	1.52	1.14	0.76	0.38	0.37	0.74	1.11	1.48	1.84	2.2	2.6	2.9
70	1.54	1.15	0.76	0.38	0.38	0.75	1.13	1.50	1.86	2.2	2.6	3.0
80	1.72	1.30	0.87	0.44	0.45	0.90	1.36	1.83	2.31	2.8	3.3	3.8
81	1.76	1.34	0.92	0.44	0.47	0.93	1.42	1.93	2.44	3.0	3.5	4.0
82	1.84	1.41	0.96	0.47	0.50	1.00	1.51	2.04	2.58	3.1	3.7	4.3
83	1.94	1.48	1.00	0.50	0.53	1.06	1.59	2.18	2.78	3.4	4.0	4.6
84	2.05	1.57	1.06	0.53	0.55	1.12	1.74	2.36	3.0	3.7	4.4	5.1
85	2.20	1.67	1.13	0.57	0.61	1.23	1.88	2.57	3.3	4.0	4.9	5.8
86	2.36	1.80	1.22	0.62	0.66	1.35	2.08	2.84	3.7	4.6	5.5	
87	2.54	1.95	1.32	0.67	0.73	1.50	2.31	3.2	4.1	5.2		
88	2.75	2.12	1.44	0.74	0.81	1.67	2.59	3.6	4.7	6.0		
89	3.01	2.31	1.58	0.82	0.89	1.86	2.91	4.1	5.6			
90	3.27	2.53	1.73	0.91	0.99	2.10	3.4	4.9				
91	3.57	2.78	1.93	1.01	1.13	2.44	4.1					
92	3.91	3.06	2.13	1.12	1.32	3.00						
93	4.29	3.38	2.37	1.26	1.64							
94	4.75	3.77	2.69	1.46								
95	5.29	4.26	3.12	1.76								
96	5.96	4.88	3.65	2.19								
97	6.78	5.68	4.42	2.90								

TABLE 14. — DENSITY OF STRONG ACIDS AT 15° IN VACUO

(According to LUNGE, ISLER, NAEF, and MARCHLEWSKY)*

In determining the weight in the air of a given volume of acid or base in this and the following tables, it must be remembered that the values here are made with allowance for the buoyancy of air (cf. pp. 13–15, 462–464).

Specific Gravity at $\frac{15°}{4°}$ (Vacuo)	Per Cent by Weight			Specific Gravity at $\frac{15°}{4°}$ (Vacuo)	Per Cent by Weight	
	HCl	HNO_3	H_2SO_4		HNO_3	H_2SO_4
1.000	0.16	0.10	0.09	1.235	37.51	31.70
1.005	1.15	1.00	0.95	1.240	38.27	32.28
1.010	2.14	1.90	1.57	1.245	39.03	32.86
1.015	3.12	2.80	2.30	1.250	39.80	33.43
1.020	4.13	3.70	3.03	1.255	40.56	34.00
1.025	5.15	4.60	3.76	1.260	41.32	34.57
1.030	6.15	5.50	4.49	1.265	42.08	35.14
1.035	7.15	6.38	5.23	1.270	42.85	35.71
1.040	8.16	7.26	5.96	1.275	43.62	36.29
1.045	9.16	8.13	6.67	1.280	44.39	36.87
1.050	10.17	8.99	7.37	1.285	45.16	37.45
1.055	11.18	9.84	8.07	1.290	45.93	38.03
1.060	12.19	10.67	8.77	1.295	46.70	38.61
1.065	13.19	11.50	9.47	1.300	47.47	39.19
1.070	14.17	12.32	10.19	1.305	48.24	39.77
1.075	15.16	13.14	10.90	1.310	49.05	40.35
1.080	16.15	13.94	11.60	1.315	49.88	40.93
1.085	17.13	14.73	12.30	1.320	50.69	41.50
1.090	18.11	15.52	12.99	1.325	51.51	42.08
1.095	19.06	16.31	13.67	1.330	52.34	42.66
1.100	20.01	17.10	14.35	1.335	53.17	43.20
1.105	20.97	17.88	15.03	1.340	54.04	43.74
1.110	21.92	18.66	15.71	1.345	54.90	44.28
1.115	22.86	19.44	16.36	1.350	55.76	44.82
1.120	23.82	20.22	17.01	1.355	56.63	45.35
1.125	24.78	20.99	17.66	1.360	57.54	45.88
1.130	25.75	21.76	18.31	1.365	58.45	46.41
1.135	26.70	22.53	18.96	1.370	59.36	46.94
1.140	27.66	23.30	19.61	1.375	60.27	47.47
1.145	28.61	24.07	20.26	1.380	61.24	48.00
1.150	29.57	24.83	20.91	1.385	62.21	48.53
1.155	30.55	25.59	21.55	1.390	63.20	49.06
1.160	31.52	26.35	22.19	1.395	64.22	49.59
1.165	32.49	27.11	22.83	1.400	65.27	50.11
1.170	33.46	27.87	23.47	1.405	66.37	50.63
1.175	34.42	28.62	24.12	1.410	67.47	51.15
1.180	35.39	29.37	24.76	1.415	68.60	51.66
1.185	36.31	30.12	25.40	1.420	69.77	52.15
1.190	37.23	30.87	26.04	1.425	70.95	52.63
1.195	38.16	31.60	26.68	1.430	72.14	53.11
1.200	39.11	32.34	27.32	1.435	73.35	53.59
1.205		33.07	27.95	1.440	74.64	54.07
1.210		33.80	28.58	1.445	75.94	54.55
1.215		34.53	29.21	1.450	77.24	55.03
1.220		35.26	29.84	1.455	78.56	55.50
1.225		36.01	30.48	1.460	79.94	55.97
1.230		36.76	31.11	1.465	81.38	56.43

* Lunge-Berl. *Chem. techn. Untersuchungsmethoden.*

TABLE 14. — DENSITY OF STRONG ACIDS AT 15° IN VACUO — *Continued*

Specific Gravity at $\frac{15°}{4°}$ (Vacuo)	Per Cent by Weight		Specific Gravity at $\frac{15°}{4°}$ (Vacuo)	Per Cent by Weight	Specific Gravity at $\frac{15°}{4°}$ (Vacuo)	Per Cent by Weight
	HNO_3	H_2SO_4		H_2SO_4		H_2SO_4
1.470	82.86	56.90	1.610	69.56	1.750	81.56
1.475	84.41	57.37	1.615	70.00	1.755	82.00
1.480	86.01	57.83	1.620	70.42	1.760	82.44
1.485	87.66	58.28	1.625	70.85	1.765	83.01
1.490	89.86	58.74	1.630	71.27	1.770	83.51
1.495	91.56	59.22	1.635	71.70	1.775	84.02
1.500	94.04	59.70	1.640	72.12	1.780	84.50
1.505	96.34	60.18	1.645	72.55	1.785	85.10
1.510	98.05	60.65	1.650	72.96	1.790	85.70
1.515	99.02	61.12	1.655	73.40	1.795	86.30
1.520	99.62	61.59	1.660	73.81	1.800	86.92
1.525		62.06	1.665	74.24	1.805	87.60
1.530		62.53	1.670	74.66	1.810	88.30
1.535		63.00	1.675	75.08	1.815	89.16
1.540		63.43	1.680	75.50	1.820	90.05
1.545		63.85	1.685	75.94	1.825	91.00
1.550		64.26	1.690	76.38	1.830	92.10
1.555		64.67	1.695	76.76	1.835	93.56
1.560		65.20	1.700	77.17	1.840	95.60
1.565		65.65	1.705	77.60	1.8405	95.95
1.570		66.09	1.710	78.04	1.8410	96.38
1.575		66.53	1.715	78.48	1.8415	97.35
1.580		66.95	1.720	78.92	1.8410	98.20
1.585		67.40	1.725	79.36	1.8405	98.52
1.590		67.83	1.730	79.80	1.8400	98.72
1.595		68.26	1.735	80.24	1.8395	98.77
1.600		68.70	1.740	80.68	1.8390	99.12
1.605		69.13	1.745	81.12	1.8385	99.31

TABLE 15. — DENSITY OF POTASSIUM AND SODIUM HYDROXIDE SOLUTIONS AT 15° C

Specific Gravity	Per Cent KOH	Per Cent NaOH	Specific Gravity	Per Cent KOH	Per Cent NaOH
1.007	0.9	0.59	1.252	27.0	22.50
1.014	1.7	1.20	1.263	28.2	23.50
1.022	2.6	1.65	1.274	28.9	24.48
1.029	3.5	2.50	1.285	29.8	25.50
1.037	4.5	3.22	1.297	30.7	26.58
1.045	5.6	3.79	1.308	31.8	27.65
1.052	6.4	4.50	1.320	32.7	28.83
1.060	7.4	5.20	1.332	33.7	30.00
1.067	8.2	5.86	1.345	34.9	31.20
1.075	9.2	6.58	1.357	35.9	32.50
1.083	10.1	7.30	1.370	36.9	33.73
1.091	10.9	8.07	1.383	37.8	35.00
1.100	12.0	8.78	1.397	38.9	36.36
1.108	12.9	9.50	1.410	39.9	37.65
1.116	13.8	10.30	1.424	40.9	39.06
1.125	14.8	11.06	1.438	42.1	40.47
1.134	15.7	11.90	1.453	43.4	42.02
1.142	16.5	12.69	1.468	44.6	43.58
1.152	17.6	13.50	1.483	45.8	45.16
1.162	18.6	14.35	1.498	47.1	47.73
1.171	19.5	15.15	1.514	48.3	48.41
1.180	20.5	16.00	1.530	49.4	50.10
1.190	21.4	16.91	1.546	50.6	.....
1.200	22.4	17.81	1.563	51.9	.....
1.210	23.3	18.71	1.580	53.2	.....
1.220	24.2	19.65	1.597	54.5	.....
1.231	25.1	20.69	1.615	55.9	.....
1.241	26.1	21.55	1.634	57.5	.....

TABLE 16. — DENSITY OF AMMONIA SOLUTIONS AT 15° C

(According to LUNGE and WIERNIK)*

Specific Gravity	Per Cent NH_3	Specific Gravity	Per Cent NH_3
1.000	0.00	0.940	15.63
0.998	0.45	0.938	16.22
0.996	0.91	0.936	16.82
0.994	1.37	0.934	17.42
0.992	1.84	0.932	18.03
0.990	2.31	0.930	18.64
0.988	2.80	0.928	19.25
0.986	3.30	0.926	19.87
0.984	3.80	0.924	20.49
0.982	4.30	0.922	21.12
0.980	4.80	0.920	21.75
0.978	5.30	0.918	22.39
0.976	5.80	0.916	23.03
0.974	6.30	0.914	23.68
0.972	6.80	0.912	24.33
0.970	7.31	0.910	24.99
0.968	7.82	0.908	25.65
0.966	8.33	0.906	26.31
0.964	8.84	0.904	26.98
0.962	9.35	0.902	27.65
0.960	9.91	0.900	28.33
0.958	10.47	0.898	29.01
0.956	11.03	0.896	29.69
0.954	11.60	0.894	30.37
0.952	12.17	0.892	31.05
0.950	12.74	0.890	31.75
0.948	13.31	0.888	32.50
0.946	13.88	0.886	33.25
0.944	14.46	0.884	34.10
0.942	15.04	0.882	34.95

* Lunge-Berl. *Chem. techn. Untersuchungsmethoden.*

TABLE 17. — TENSION OF WATER VAPOR ACCORDING TO REGNAULT

Degrees C	Tension in Millimeters	Degrees C	Tension in Millimeters	Degrees C	Tension in Millimeters
−2.0	3.955	+2.0	5.302	+6.0	6.998
1.9	3.985	2.1	5.340	6.1	7.047
1.8	4.016	2.2	5.378	6.2	7.095
1.7	4.047	2.3	5.416	6.3	7.144
1.6	4.078	2.4	5.454	6.4	7.193
1.5	4.109	2.5	5.491	6.5	7.242
1.4	4.140	2.6	5.530	6.6	7.292
1.3	4.171	2.7	5.569	6.7	7.342
1.2	4.203	2.8	5.608	6.8	7.392
1.1	4.235	2.9	5.647	6.9	7.442
1.0	4.267	3.0	5.687	7.0	7.492
0.9	4.299	3.1	5.727	7.1	7.544
0.8	4.331	3.2	5.767	7.2	7.595
0.7	4.364	3.3	5.807	7.3	7.647
0.6	4.397	3.4	5.848	7.4	7.699
0.5	4.430	3.5	5.889	7.5	7.751
0.4	4.463	3.6	5.930	7.6	7.804
0.3	4.497	3.7	5.972	7.7	7.857
0.2	4.531	3.8	6.014	7.8	7.910
0.1	4.565	3.9	6.055	7.9	7.964
0.0	4.600	4.0	6.097	8.0	8.017
+0.1	4.633	4.1	6.140	8.1	8.072
0.2	4.667	4.2	6.183	8.2	8.126
0.3	4.700	4.3	6.226	8.3	8.181
0.4	4.733	4.4	6.270	8.4	8.236
0.5	4.767	4.5	6.313	8.5	8.291
0.6	4.801	4.6	6.357	8.6	8.347
0.7	4.836	4.7	6.401	8.7	8.404
0.8	4.871	4.8	6.445	8.8	8.461
0.9	4.905	4.9	6.490	8.9	8.517
1.0	4.940	5.0	6.534	9.0	8.574
1.1	4.975	5.1	6.580	9.1	8.632
1.2	5.011	5.2	6.625	9.2	8.690
1.3	5.047	5.3	6.671	9.3	8.748
1.4	5.082	5.4	6.717	9.4	8.807
1.5	5.118	5.5	6.763	9.5	8.865
1.6	5.155	5.6	6.810	9.6	8.925
1.7	5.191	5.7	6.857	9.7	8.985
1.8	5.228	5.8	6.904	9.8	9.045
1.9	5.265	5.9	6.951	9.9	9.105

TABLE 17. — TENSION OF WATER VAPOR ACCORDING TO REGNAULT — *Continued*

Degrees C	Tension in Millimeters	Degrees C	Tension in Millimeters	Degrees C.	Tension in Millimeters
+10.0	9.165	+14.0	11.908	+18.0	15.357
10.1	9.227	14.1	11.986	18.1	15.454
10.2	9.288	14.2	12.064	18.2	15.552
10.3	9.350	14.3	12.142	18.3	15.650
10.4	9.412	14.4	12.220	18.4	15.747
10.5	9.474	14.5	12.298	18.5	15.845
10.6	9.537	14.6	12.378	18.6	15.945
10.7	9.601	14.7	12.458	18.7	16.045
10.8	9.665	14.8	12.538	18.8	16.145
10.9	9.728	14.9	12.619	18.9	16.246
11.0	9.792	15.0	12.699	19.0	16.346
11.1	9.857	15.1	12.781	19.1	16.449
11.2	9.923	15.2	12.864	19.2	16.552
11.3	9.989	15.3	12.947	19.3	16.655
11.4	10.054	15.4	13.029	19.4	16.758
11.5	10.120	15.5	13.112	19.5	16.861
11.6	10.187	15.6	13.197	19.6	16.967
11.7	10.255	15.7	13.281	19.7	17.073
11.8	10.322	15.8	13.366	19.8	17.179
11.9	10.389	15.9	13.451	19.9	17.285
12.0	10.457	16.0	13.536	20.0	17.391
12.1	10.526	16.1	13.623	20.1	17.500
12.2	10.596	16.2	13.710	20.2	17.608
12.3	10.665	16.3	13.797	20.3	17.717
12.4	10.734	16.4	13.885	20.4	17.826
12.5	10.804	16.5	13.972	20.5	17.935
12.6	10.875	16.6	14.062	20.6	18.047
12.7	10.947	16.7	14.151	20.7	18.159
12.8	11.019	16.8	14.241	20.8	18.271
12.9	11.090	16.9	14.331	20.9	18.383
13.0	11.162	17.0	14.421	21.0	18.495
13.1	11.235	17.1	14.513	21.1	18.610
13.2	11.309	17.2	14.605	21.2	18.724
13.3	11.383	17.3	14.697	21.3	18.839
13.4	11.456	17.4	14.790	21.4	18.954
13.5	11.530	17.5	14.882	21.5	19.069
13.6	11.605	17.6	14.977	21.6	19.187
13.7	11.681	17.7	15.072	21.7	19.305
13.8	11.757	17.8	15.167	21.8	19.423
13.9	11.832	17.9	15.262	21.9	19.541

TABLE 17. — TENSION OF WATER VAPOR ACCORDING TO REGNAULT — *Concluded*

Degrees C	Tension in Millimeters	Degrees C	Tension in Millimeters	Degrees C	Tension in Millimeters
+22.0	19.659	+26.5	25.738	+31.0	33.405
22.1	19.780	26.6	25.891	31.1	33.596
22.2	19.901	26.7	26.045	31.2	33.787
22.3	20.022	26.8	26.198	31.3	33.980
22.4	20.143	26.9	26.351	31.4	34.174
22.5	20.265	27.0	26.505	31.5	34.368
22.6	20.389	27.1	26.663	31.6	34.564
22.7	20.514	27.2	26.820	31.7	34.761
22.8	20.639	27.3	26.978	31.8	34.959
22.9	20.763	27.4	27.136	31.9	35.159
23.0	20.888	27.5	27.294	32.0	35.359
23.1	21.016	27.6	27.455	32.1	35.559
23.2	21.144	27.7	27.617	32.2	35.760
23.3	21.272	27.8	27.778	32.3	35.962
23.4	21.400	27.9	27.939	32.4	36.165
23.5	21.528	28.0	28.101	32.5	36.370
23.6	21.659	28.1	28.267	32.6	36.576
23.7	21.790	28.2	28.433	32.7	36.783
23.8	21.921	28.3	28.599	32.8	36.991
23.9	22.053	28.4	28.765	32.9	37.200
24.0	22.184	28.5	28.931	33.0	37.410
24.1	22.319	28.6	29.101	33.1	37.621
24.2	22.453	28.7	29.271	33.2	37.832
24.3	22.588	28.8	29.441	33.3	38.045
24.4	22.723	28.9	29.612	33.4	38.258
24.5	22.858	29.0	29.782	33.5	38.473
24.6	22.996	29.1	29.956	33.6	38.689
24.7	23.135	29.2	30.131	33.7	38.906
24.8	23.273	29.3	30.305	33.8	39.124
24.9	23.411	29.4	30.479	33.9	39.344
25.0	23.550	29.5	30.654	34.0	39.565
25.1	23.692	29.6	30.833	34.1	39.786
25.2	23.834	29.7	31.011	34.2	40.007
25.3	23.976	29.8	31.190	34.3	40.230
25.4	24.119	29.9	31.369	34.4	40.455
25.5	24.261	30.0	31.548	34.5	40.680
25.6	24.406	30.1	31.729	34.6	40.907
25.7	24.552	30.2	31.911	34.7	41.135
25.8	24.697	30.3	32.094	34.8	41.364
25.9	24.842	30.4	32.278	34.9	41.595
26.0	24.988	30.5	32.463	35.0	41.827
26.1	25.138	30.6	32.650		
26.2	25.288	30.7	32.837		
26.3	25.438	30.8	33.026		
26.4	25.588	30.9	33.215		

TABLE 18. — HEATS OF COMBUSTION OF 1 L OF GAS MEASURED AT 0° AND 760 MM BAROMETRIC PRESSURE

Gas	Weight of 1 L in Grams	Referred to Gaseous Water Calories	Referred to Liquid Water Calories
Carbon monoxide.	1.25016	2,560	3,034
Hydrogen........	0.09004	2,595	3,077
Methane.........	0.71488	8,505	9,469
Ethylene.........	1.25899	14,018	14,989
Propylene........	1.93660	21,226	22,720
Benzene-gas......	3.48428	(?)33,750	(?)35,198
Acetylene........	1.18080	13,582	14,073
Generator-gas....		about 900	about 1,000
Water-gas........		" 3,386	" 3,700
Dowson gas......		" 1,400	....
Illuminating-gas..		" 5,000	" 5,500

The values in the above table are based upon Thomsen's measurements and only in the case of benzene is the theoretical density used.*

TABLE 18A

At the seventh General Conference on Weights and Measures the following standard temperatures were adopted for preparing an international temperature scale.

Boiling point of oxygen..................................	−182.97° C
Melting point of ice.....................................	0.00
Boiling point of water...................................	100.00
Melting point of sulfur..................................	444.60
Melting point of silver..................................	960.5
Melting point of gold....................................	1063

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* Julius Thomsen, *Thermochem. Untersuchungen* (1882), Vol. II, pp. 56, 85, 107, and Vol. IV, p. 254.

$$CO + O = CO_2 + 67{,}960 \text{ cals.}$$
$$H_2 + O = H_2O + 68{,}357 \text{ cals.}$$
$$CH_4 + 4\,O = 2\,H_2O + CO_2 + 211{,}930 \text{ cals.}$$
$$C_2H_4 + 6\,O = 2\,H_2O + 2\,CO_2 + 333{,}350 \text{ cals.}$$
$$C_3H_6 + 9\,O = 3\,H_2O + 3\,CO_2 + 492{,}740 \text{ cals.}$$
$$C_2H_6 + 15\,O = 3\,H_2O + 6\,CO_2 + 787{,}950 \text{ cals.}$$
$$C_2H_2 + 5\,O = H_2O + 2\,CO_2 + 310{,}450 \text{ cals.}$$

TABLE 19. — MELTING POINTS OF THE CHEMICAL ELEMENTS[1]

Element	C	F	Element	C	F
Helium	<−271	<−456	Neodymium	840?	1544
Hydrogen	−259	−434	Arsenic	850?	1562
Neon	−253?	−423	Barium	850	1562
Fluorine	−223	−369	Praseodymium	940?	1724
Oxygen	−218	−360	Germanium	958	1756
Nitrogen	−210	−346	SILVER	960.5	1761
Argon	−188	−306	GOLD	1063.0	1945.5
Krypton	−169	−272	COPPER	1083.0	1981.5
Xenon	−140	−220	Manganese	1260	2300
Chlorine	−101.5	−150.7	Samarium	1300–1400	2370–2550
Mercury	− 38.9	− 38.0	Beryllium		
Bromine	− 7.3	+ 18.9	(glucinum)	1350?	2462
Cesium	+ 26	79	Scandium	?	
Gallium	30	86	Silicon	1420	2588
Rubidium	38	100	NICKEL	1452	2646
Phosphorus	44	111.2	Cobalt	1480	2696
Potassium	62.3	144	Yttrium	1490	2714
Sodium	97.5	207.5	Chromium	1520	2768
Iodine	113.5	236.3	IRON	1530	2786
Sulfur	S_{I} 112.8	235.0	PALLADIUM	1549	2820
	S_{II} 119.2	246.6	Zirconium	1700?	3090
	S_{III} 106.8	224.2	Columbium		
Indium	155	311	(Niobium)	1700?	3090
Lithium	186	367		>1700	>3090
Selenium	217–220	422–428	Thorium	<Pt	<Pt
TIN	231.9	449.4	Vanadium	1720	3128
Bismuth	271	520	PLATINUM	1755	3191
Thallium	302	576	Ytterbium	?	
CADMIUM	320.9	609.6	Titanium	1800	3272
LEAD	327.4	621.3	Uranium	<1850	<3362
ZINC	419.4	786.9	Rhodium	1950	3542
Tellurium	452	846	Boron	2200–2500?	4000–4500
ANTIMONY	630.0	1166	Iridium	2350?	4262
Cerium	640	1184	Ruthenium	2450?	4442
Magnesium	651	1204	Molybdenum	2500?	4500
ALUMINUM	658.7	1217.7	Osmium	2700?	4900
Radium	700	1292	Tantalum	2850	5160
Calcium	810	1490	TUNGSTEN	3000	5430
Lanthanum	810?	1490	Carbon	>3600	>6500
Strontium	>Ca<Ba?			for p. = 1 at.	for p. = 1 at

Reproduced from Circular No. 35 (2nd edition) of U. S. Bureau of Standards.

TABLE 20. — APPROXIMATE TEMPERATURES BY COLORS

	Cent.	Fahr.
First visible red	525	977
Dull red........	700	1292
Cherry red.....	900	1652
Dull orange....	1100	2012
White..........	1300	2372
Dazzling white.	1500	2732

TABLE 21. — DENSITY OF PHOSPHORIC ACID AT 17.5°

Specific Gravity	Per Cent P_2O_5	Per Cent H_3PO_4	Specific Gravity	Per Cent P_2O_5	Per Cent H_3PO_4	Specific Gravity	Per Cent P_2O_5	Per Cent H_3PO_4
1.809	68.0	93.67	1.462	46.0	63.37	1.208	24.0	33.06
1.800	67.5	92.99	1.455	45.5	62.68	1.203	23.5	32.37
1.792	67.0	92.30	1.448	45.0	61.99	1.198	23.0	31.68
1.783	66.5	91.61	1.441	44.5	61.30	1.193	22.5	30.99
1.775	66.0	90.92	1.435	44.0	60.61	1.188	22.0	30.31
1.766	65.5	90.23	1.428	43.5	59.92	1.183	21.5	29.62
1.758	65.0	89.54	1.422	43.0	59.23	1.178	21.0	28.93
1.750	64.5	88.85	1.415	42.5	58.55	1.174	20.5	28.24
1.741	64.0	88.16	1.409	42.0	57.86	1.169	20.0	27.55
1.733	63.5	87.48	1.402	41.5	57.17	1.164	19.5	26.86
1.725	63.0	86.79	1.396	41.0	56.48	1.159	19.0	26.17
1.717	62.5	86.10	1.389	40.5	55.79	1.155	18.5	25.48
1.709	62.0	85.41	1.383	40.0	55.10	1.150	18.0	24.80
1.701	61.5	84.72	1.377	39.5	54.41	1.145	17.5	24.11
1.693	61.0	84.03	1.371	39.0	53.72	1.140	17.0	23.42
1.685	60.5	83.34	1.365	38.5	53.04	1.135	16.5	22.73
1.677	60.0	82.65	1.359	38.0	52.35	1.130	16.0	22.04
1.669	59.5	81.97	1.354	37.5	51.66	1.126	15.5	21.35
1.661	59.0	81.28	1.348	37.0	50.97	1.122	15.0	20.66
1.653	58.5	80.59	1.342	36.5	50.28	1.118	14.5	19.97
1.645	58.0	79.90	1.336	36.0	49.59	1.113	14.0	19.28
1.637	57.5	79.21	1.330	35.5	48.90	1.109	13.5	18.60
1.629	57.0	78.52	1.325	35.0	48.21	1.104	13.0	17.91
1.621	56.5	77.83	1.319	34.5	47.52	1.100	12.5	17.22
1.613	56.0	77.14	1.314	34.0	46.84	1.096	12.0	16.53
1.605	55.5	76.45	1.308	33.5	46.15	1.091	11.5	15 84
1.597	55.0	75.77	1.303	33.0	45.46	1.087	11.0	15.15
1.589	54.5	75.08	1.298	32.5	44.77	1.083	10.5	14.46
1.581	54.0	74.39	1.292	32.0	44.08	1.079	10.0	13.77
1.574	53.5	73.70	1.287	31.5	43.39	1.074	9.5	13.09
1.566	53.0	73.01	1.281	31.0	42.70	1.070	9.0	12.40
1.559	52.5	72.32	1.276	30.5	42.01	1.066	8.5	11.71
1.551	52.0	71.63	1.271	30.0	41.33	1.062	8.0	11.02
1.543	51.5	70.94	1.265	29.5	40.64	1.058	7.5	10.33
1.536	51.0	70.26	1.260	29.0	39.95	1.053	7.0	9.64
1.528	50.5	69.57	1.255	28.5	39.26	1.049	6.5	8.95
1.521	50.0	68.88	1.249	28.0	38.57	1.045	6.0	8.26
1.513	49.5	68.19	1.244	27.5	37.88	1.041	5.5	7.57
1.505	49.0	67.50	1.239	27.0	37.19	1.037	5.0	6.89
1.498	48.5	66.81	1.233	26.5	36.50	1.033	4.5	6.20
1.491	48.0	66.12	1.228	26.0	35.82	1.029	4.0	5.51
1.484	47.5	65.43	1.223	25.5	35.13	1.025	3.5	4.82
1.476	47.0	64.75	1.218	25.0	34.44	1.021	3.0	4.13
1.469	46.5	64.06	1.213	24.5	33.75	1.017	2.5	3.44

TABLE 22. — DENSITY OF ACETIC ACID AT 15°

Specific Gravity	Per Cent $H.C_2H_3O_2$	Specific Gravity	Per Cent $H.C_2H_3O_2$	Specific Gravity	Per Cent $H.C_3H_2O_2$	Specific Gravity	Per Cent $H.C_2H_3O_2$
0.9992	0	1.0363	26	1.0623	51	1.0747	76
1.0007	1	1.0375	27	1.0631	52	1.0748	77
1.0022	2	1.0388	28	1.0638	53	1.0748	78
1.0037	3	1.0400	29	1.0646	54	1.0748	79
1.0052	4	1.0412	30	1.0653	55	1.0748	80
1.0067	5	1.0424	31	1.0660	56	1.0747	81
1.0083	6	1.0436	32	1.0666	57	1.0746	82
1.0098	7	1.0447	33	1.0673	58	1.0744	83
1.0113	8	1.0459	34	1.0679	59	1.0742	84
1.0127	9	1.0470	35	1.0685	60	1.0739	85
1.0142	10	1.0481	36	1.0691	61	1.0736	86
1.0157	11	1.0492	37	1.0697	62	1.0731	87
1.0171	12	1.0502	38	1.0702	63	1.0726	88
1.0185	13	1.0513	39	1.0707	64	1.0720	89
1.0200	14	1.0523	40	1.0712	65	1.0713	90
1.0214	15	1.0533	41	1.0717	66	1.0705	91
1.0228	16	1.0543	42	1.0721	67	1.0696	92
1.0242	17	1.0552	43	1.0725	68	1.0686	93
1.0256	18	1.0562	44	1.0729	69	1.0674	94
1.0270	19	1.0571	45	1.0733	70	1.0660	95
1.0284	20	1.0580	46	1.0737	71	1.0644	96
1.0298	21	1.0589	47	1.0740	72	1.0625	97
1.0311	22	1.0598	48	1.0742	73	1.0604	98
1.0324	23	1.0607	49	1.0744	74	1.0580	99
1.0337	24	1.0615	50	1.0746	75	1.0553	100
1.0350	25						

TABLE 23. — USEFUL DATA OF THE MORE IMPORTANT INORGANIC COMPOUNDS*

Substance	Formula	Molecular or Atomic Weight	Weight in 1 ml of *N* solution	Solubility in 100 Gms. Water
Acetic acid	$HC_2H_3O_2$	60.03	.06003	
Aluminum	Al	27.10	.009033	
chloride	Al_2Cl_6	266.96	.04449	$69.87^{15°}$
chloride	$Al_2Cl_6 \cdot 12H_2O$	483.15	.08053	40
oxide	Al_2O_3	102.20	.01703	insol.
sulfate	$Al_2(SO_4)_3$	342.38	.05706	$36.1^{20°}$
sulfate	$Al_2(SO_4)_3 \cdot 18H_2O$	666.67	.1111	87
Ammonia	NH_3	17.03	.01703	
Ammonium	NH_4	18.04	.01804	
chloride	NH_4Cl	53.50	.05350	$29.4^{0°}$
hydroxide	NH_4OH	35.05	.03505	
nitrate	NH_4NO_3	80.05	.08005	$118^{0°}$
sulfate	$(NH_4)_2SO_4$	132.14	.06607	$71^{0°}$
Antimony	Sb	121.77	.06090	
Arsenic	As	74.96	.03748	
oxide	As_2O_5	229.92	.03832[1]	150
Arsenous oxide	As_2O_3	197.92	.03299	
Arsenious oxide	As_2O_3	197.92	.04948[3]	
Barium	Ba	137.37	.06868	
carbonate	$BaCO_3$	197.37	.09868	
chloride	$BaCl_2$	208.29	.1041	
chloride	$BaCl_2 \cdot 2H_2O$	244.32	.12212	$36.2^{0°}$
hydroxide	$Ba(OH)_2$	171.38	.08569	
hydroxide	$Ba(OH)_2 \cdot 8H_2O$	315.51	.1577	$5.56^{15°}$
sulfate	$BaSO_4$	233.44	.1167	$.000172^{0°}$
oxide	BaO	153.37	.07668	$1.5^{0°}$
peroxide	BaO_2	169.37	.08469	insol.
Bromine	Br	79.92	.07992	$4.17^{0°}$
Cadmium carbonate	$CdCO_3$	172.40	.08620	insol.
chloride	$CdCl_2$	183.32	.09166	$140^{20°}$
chloride	$CdCl_2 \cdot 2H_2O$	219.35	.1097	$168^{20°}$
sulfide	CdS	144.47	.07223	insol.
Calcium	Ca	40.00	.02000	
carbonate	$CaCO_3$	100.07	.05003	.0013
chloride	$CaCl_2$	110.99	.055495	$59.5^{0°}$
chloride	$CaCl_2 \cdot 6H_2O$	219.086	.10954	$117.4^{0°}$
hydroxide	$Ca(OH)_2$	74.09	.03704	$.17^{0°}$
oxide	CaO	56.07	.02803	$.13^{0°}$
sulfate	$CaSO_4$	136.14	.06807	$.179^{0°}$
sulfide	CaS	72.14	.03607	$.15^{10°}$
Carbon	C	12.005	.00300	insol.
dioxide	CO_2	44.00	.02200[1]	179.67 ml.$^{0°}$
Chlorine	Cl	35.46	.03546	150 ml.$^{0°}$
Chromic anhydride	CrO_3	100.00	.033333[3]	$163.4^{0°}$
oxide	Cr_2O_3	152.00	.02533[3]	insol.
Citric acid	$H_3C_6H_5O_7$	192.06	.06402	133.
Cobalt	Co	58.97	.02948	
Copper	Cu	63.57	.03178[4]	
oxide	CuO	79.57	.07957	
sulfate	$CuSO_4$	159.63	.1596	$20^{0°}$
sulfate	C	249.71	.2497	$31.61^{0°}$
sulfide	CuS	95.63	.04781	.000033

[1] Precipitation reagents. [2] Acids and bases. [3] Oxidizing and reducing agents.
[4] In the iodide method for determining copper the milliequivalent is 0.06357.
* Compiled and arranged by R. M. Meiklejohn.

TABLE 23. — USEFUL DATA OF THE MORE IMPORTANT INORGANIC COMPOUNDS — *Continued*

Substance	Formula	Molecular or Atomic Weight	Weight in 1 ml of *N* solution	Solubility in 100 Gms. Water
Cyanogen	CN	26.005	.02600	
Ferric oxide	Fe_2O_3	159.68	.07984[3]	
Ferrous oxide	FeO	71.84	.07184[3]	insol.
sulfate	$FeSO_4$	151.90	.1519[3]	
sulfate	$FeSO_4 \cdot 7H_2O$	278.01	.2780[3]	$32.8^{0°}$
ammon'm sulfate	$FeSO_4(NH_4)_2SO_4 \cdot 6H_2O$	392.14	.3921	$18^{0°}$
Hydrobromic acid	HBr	80.928	.08093	$221.2^{0°}$
Hydrochloric acid	HCl	36.47	.03647	$82.5^{10°}$
Hydrocyanic acid	HCN	27.02	.02702	
Hydrofluoric acid	HF	20.01	.02001	264
Hydriodic acid	HI	127.93	.1279	
Hydrogen peroxide	H_2O_2	34.016	.01700	
Hydrogen sulfide	H_2S	34.076	.01704	437 ml.$^{0°}$
Iodine	I	126.92	.1269	$.0182^{11°}$
Iron	Fe	55.84	.05584	
Lead	Pb	207.20	.1036	
carbonate	$PbCO_3$	267.20	.1336	.00198
chromate	$PbCrO_4$	323.20	.1616	$.00002^{18°}$
oxide	PbO	223.20	.1116	
peroxide	PbO_2	239.20	.1196	
sulfide	PbS	239.26	.1196	.0001
Magnesium	Mg	24.32	.01216	
carbonate	$MgCO_3$	84.32	.04216	.0106
chloride	$MgCl_2$	95.24	.04762	$52.2^{0°}$
chloride	$MgCl_2 \cdot 6H_2O$	203.34	.1017	167
oxide	MgO	40.32	.02016	.00062
sulfate	$MgSO_4$	120.38	.06019	$26.9^{0°}$
sulfate	$MgSO_4 \cdot 7H_2O$	246.49	.1232	$76.9^{0°}$
Malic acid	$H_2C_4H_4O_5$	134.06	.06703	
Manganese	Mn	54.93	.02746	
chloride	$MnCl_2$	125.85	.06292	$62.16^{10°}$
peroxide	MnO_2	86.93	.04346	insol.
sulfate	$MnSO_4$	150.99	.07549	$53.2^{0°}$
Mercuric chloride	$HgCl_2$	271.52	.1358	$5.73^{0°}$
Nickel	Ni	58.68	.02934	
Nitric acid	$HNO_3 \cdot$	63.02	.06302[2]	
Nitric acid	HNO_3	63.02	.02101[3]	
Nitrogen trioxide	N_2O_3	76.02	.01900[3]	
pentoxide	N_2O_5	108.02	.05401[2]	
pentoxide	N_2O_5	108.02	.01803[3]	
Nitrous acid	HNO_2	47.02	.04702	
Nitrogen	N	14.01	.01401	
Oxalic acid	$H_2C_2O_4$	90.02	.04501	
Oxalic acid	$H_2C_2O_4 \cdot 2H_2O$	126.05	.06302	$4.9^{0°}$
Phosphoric acid	H_3PO_4	98.06	.09806[2]	v. sol.
Phosphoric acid	H_3PO_4	98.06	$.04903_2$	v. sol.
Phosphoric acid	H_3PO_4	98.06	.03268	v. sol.
Potassium	K	39.10	.03910	
bicarbonate	$KHCO_3$	100.11	.1001	$22.4^{0°}$
bitartrate	$KHC_4H_4O_6$	188.14	.1881	$.37^{0°}$
bromide	KBr	119.02	.11902	$53.48^{0°}$
carbonate	K_2CO_3	138.20	.06910	$89.4^{0°}$
chlorate	$KClO_3$	122.56	.02043[3]	3.3^{0}_{4}

[1] Precipitation reagents. [2] Acids and bases. [3] Oxidizing and reducing agents.
M Methyl orange. P. Phenolphthalein. Temp. C.

TABLE 23. — USEFUL DATA OF THE MORE IMPORTANT INORGANIC COMPOUNDS — *Concluded*

Substance	Formula	Molecular or atomic weight	Weight in 1 ml of N solution	Solubility in 100 Gms. Water[4]
Potassium chloride..	KCl	74.56	.07456	28.5$^{0°}$
chromate.........	K_2CrO_4	194.20	.06473[3]	61.5$^{0°}$
chloroplatinate...	K_2PtCl_6	486.16	......	insol. in alc.
cyanide...........	KCN	65.11	.06511[5]	v. sol.
dichromate.......	$K_2Cr_2O_7$	294.20	.1471[2]	4.9$^{0°}$
dichromate.......	$K_2Cr_2O_7$	294.20	.04903[3]	4.9$^{0°}$
ferrocyanide......	$K_4Fe(CN)_6$	368.30	.3683	
ferrocyanide......	$K_4Fe(CN)_6{\cdot}3H_2O$	422.35	.4223	27.8$^{12°}$
hydroxide........	KOH	56.11	.05611	107$^{15°}$
iodate............	KIO_3	214.02	.03567	4.74$^{0°}$
iodide............	KI	166.03	.1660	126.1$^{0°}$
nitrate...........	KNO_3	101.11	.03370	13.3$^{0°}$
nitrite...........	KNO_2	85.11	.08511	300$^{15.5°}$
oxide.............	K_2O	94.20	.04710	v. sol.
permanganate....	$KMnO_4$	158.03	.03161	2.83$^{0°}$
sulfide............	K_2S	110.26	.05513	sol.
sulfocyanate......	$KCNS$	97.18	.09718	177.2$^{0°}$
tartrate..........		226.23	.1131	sol.
Silver.............	Ag	107.88	.1079	
nitrate...........	$AgNO_3$	169.89	.1699	122$^{0°}$
Sodium.............	Na	23.00	.02300	
bromide..........	$NaBr$	102.92	.1029	79.5$^{0°}$
bicarbonate......	$NaHCO_3$	84.01	.08401	6.90$^{0°}$
carbonate........	Na_2CO_3	106.00	.05300	7.1$^{0°}$
chloride..........	$NaCl$	58.46	.05846	35.7$^{0°}$
cyanide..........	$NaCN$	49.01	.04901	sol.
hydroxide........	$NaOH$	40.01	.04001	133.3$^{18°}$
iodide...........	NaI	149.92	.1499[1]	158.7$^{0°}$
nitrate..........	$NaNO_3$	85.01	.02834	72.9$^{0°}$
nitrite...........	$NaNO_2$	69.01	.06901	83.3$^{20°}$
oxalate...........	$Na_2C_2O_4$	134.00	.06700	3.22$^{15.5°}$
oxide.............	Na_2O	62.00	.03100	decomp.
phosphate (mono)..	NaH_2PO_4	120.06[2]	.1201	v. sol.
phosphate (disod)..	Na_2HPO_4	142.05[2]	.1421	
phosphate (disod)..	$Na_2HPO_4{\cdot}12H_2O$	358.24[2]	.3582	6.3$^{0°}$
phosphate (trisod).	Na_3PO_4	164.04[2]	.1640	
sulfide............	Na_2S	78.06	.03903	15.4$^{10°}$
thiosulfate.........	$Na_2S_2O_3{\cdot}5H_2O$	248.20	.2482	74.7$^{0°}$
Stannous chloride....	$SnCl_2$	189.62	.09481	83.9$^{0°}$
chloride...........	$SnCl_2{\cdot}2H_2O$	225.65	.1128	118.7$^{0°}$
oxide..............	SnO	134.70	.06735	insol.
Sulfur dioxide........	SO_2	64.06	.03203	7979 ml.$^{0°}$
trioxide............	SO_3	80.06	.04003	
Sulfuric acid.........	H_2SO_4	98.076	.04904	
Tartaric acid........	$H_2C_4H_4O_6$	150.05	.07503	115$^{0°}$
Tin.................	Sn	118.70	.05935	
Zinc................	Zn	65.37	.03268	
carbonate..........	$ZnCO_3$	125.37	.06268	.001$^{15°}$
chloride...........	$ZnCl_2$	136.29	.06814	209$^{0°}$
oxide..............	ZnO	81.37	.04068	.001
sulfate	$ZnSO_4$	161.43	.08071	43.02$^{0°}$
sulfate	$ZnSO_4{\cdot}7H_2O$	287.54	.1438	115.2$^{0°}$
sulfide.............	ZnS	97.43	.04871	.00069

[1] Precipitation reagents. [2] Acids and bases. [3] Oxidizing and reducing agents.

[4] The small superior numbers in the last column refer to the temperature in degrees Centigrade.

[5] In the Liebig KCN titration and in the determination of nickel the milli-equivalent is 0.1302.

TABLE 24. — COMPARISON OF METRIC AND CUSTOMARY UNITS (U. S.)

LENGTH

1 millimeter, mm = 0.03937 inch.	1 inch = 25.4 millimeters.
1 centimeter, cm = 0.39371 inch.	1 inch = 2.5400 centimeters.
1 meter, m = 3.2808 feet.	1 foot = 0.30480 meter.
1 meter = 1.0936 yards.	1 yard = 0.91440 meter.
1 kilometer = 0.62137 (U.S.) mile.	1 mile = 1.6094 kilometers.

AREAS

1 square millimeter, sq mm = 0.00155 sq in.	1 sq in = 645.16 sq mm.
1 square centimeter, sq cm = 0.1550 sq in.	1 sq in = 6.452 sq cm.
1 square meter, sq m = 10.764 sq ft.	1 sq ft = 0.0929 sq m.
1 square meter = 1.196 sq yd.	1 sq yd = 0.8361 sq m.
1 square kilometer = 0.3861 sq mi.	1 sq mi = 2.5900 sq km.
1 hectare = 2.471 acres.	1 acre = 0.4047 hectare.

VOLUMES

1 cubic millimeter, cu mm = 0.000061 cu in.	1 cu in = 16,387 cu mm.
1 cubic centimeter, ml = 0.06103 cu in.	1 cu in = 16.387 ml.
1 cubic meter = 35.314 cu ft.	1 cu ft = 0.02832 cu m.
= 61,028 cu in.	= 28.32 liters.
1 cubic meter = 1.3079 cu yd.	1 cu yd = 0.7645 cu m.

CAPACITIES

1 cubic centimeter, ml = 0.03381 (U.S.) liquid oz.	1 ounce = 29.574 ml.
1 cubic centimeter = 0.2705 (U.S.) apothecaries' dram.	1 dram = 3.6967 ml.
1 cubic centimeter = 0.8115 (U.S.) apothecaries' scruple.	1 scruple = 1.2322 ml.
1 liter = 1.05668 (U.S.) liquid qts.	1 quart = 0.94636 liter.
1 liter = 0.26417 (U.S.) gallon.	1 gallon = 3.78543 liters.
1 liter = 0.11351 (U.S.) peck.	1 peck = 8.80982 liters.
1 hectoliter = 2.83774 (U.S.) bushels.	1 bushel = 0.35239 hectoliter.

MASSES

1 gram = 15.432 grains.	1 grain = 0.06480 gram.
1 gram = 0.03527 avoirdupois ounce.	1 ounce (av.) = 28.350 grams = 437.5 grains.
1 gram = 0.03215 troy ounce.	1 ounce (troy) = 31.103 grams = 480 grains.
1 kilogram = 2.2046 pounds (av.).	1 pound (av.) = 0.4536 kilogram.
1 kilogram = 2.6792 pounds (troy).	1 pound (troy) = 0.37324 kilogram.

AVOIRDUPOIS WEIGHT

The system of weights in ordinary use by which common or heavy articles are weighed.

16 drams	= 1 ounce	= 28.35 grams.
16 ounces	= 1 pound	= 453.59 grams.
25 pounds	= 1 quarter	= 11.34 kilograms.
4 quarters	= 1 hundred weight	= 45.359 kilograms.

APOTHECARIES' WEIGHT

The system of weights sometimes employed in weighing medicines.

1 grain		= 0.0648 gram.
20 grains	= 1 scruple	= 1.296 grams.
3 scruples	= 1 drachm	= 3.888 grams.
8 drachms	= 1 ounce	= 31.10 grams.
12 ounces	= 1 pound	= 373.23 grams.

1 apothecaries' (or troy) pound contains 5760 grains.
1 apothecaries' (or troy) ounce contains 480 grains.

FLUID MEASURE

1 minim		0.06161	cubic centimeter.
60 minims	= 1 fluid drachm	3.696	cubic centimeters.
8 fluid drachms	= 1 fluid ounce	29.573	cubic centimeters.
16 fluid ounces	= 1 pint	473.18	cubic centimeters.
8 pints	= 1 gallon	3.785	liters.

1 gallon contains 231 cubic inches.

The minim, fluid drachm, fluid ounce and pint are the fluid measures sometimes employed by apothecaries.

Useful Approximations

1 molecular weight in grams of a gas = 22.4 liters.
1 molecular weight in pounds of a gas = 359 cubic feet.

To find temperatures on the absolute scales, which starts at the "absolute" zero, add 273° to the reading of the Centigrade thermometer or 459.4° to the reading of the Fahrenheit thermometer. The so-called "standard conditions" for measuring gases (0° and 760 mm of Hg pressure) are 273° (absolute) and 760 mm or 491.4° F (absolute) and 29.92 in. of mercury pressure or 14.7 lb per sq in.

SPECIFIC GRAVITIES OF COMMON SUBSTANCES

Aluminum	2.7	Lead	11.3	Quartz	2.66
Brass	8.4	Marble	2.7	Rock Salt	2.15
Cast iron	7.3	Mercury	13.6	Silver	10.5
Glass	2.6	Nickel	8.7	Steel	7.8
Gold	19.3	Platinum	21.4	Sulfur	2.05
Ivory	1.9	Porcelain	2.4	Zinc	7.10

TABLES FOR CALCULATING ANALYSES

DIRECTIONS FOR USING THE TABLES

Computations of Gravimetric Analysis. — The methods of computing the results in gravimetric work have been shown in the text. In the so-called *direct analysis* it is assumed that all the desired element in the original substance is converted into a weighed precipitate of which a known fraction consists of the element in question. The fraction, usually expressed as a decimal, which represents the amount of an element A in one of its compounds is commonly called the *chemical factor*: It represents the weight of A in one part by weight of the compound, independent of what unit of weight is used.

Thus, to be specific, 1 g of silver chloride contains 0.7526 g of silver; 1 lb of silver chloride contains 0.7526 lb of silver. If p grams of silver chloride are obtained from s grams of original substance, then 0.7526 p is the weight of silver in the sample taken and $\frac{0.7526\, p \times 100}{s}$ = per cent of silver in the substance analyzed. The general rule for computing a direct gravimetric analysis is as follows: Multiply the weight of the precipitate by 100 times the chemical factor and divide by the weight of the original substance. Using the notation as above:

$$\frac{p \times \text{chem. factor} \times 100}{s} = \text{desired percentage}$$

A table of chemical factors is given on the following pages. The use of the table may be illustrated by an example:

From 0.5 g of arsenic ore, 0.4761 g of $Mg_2As_2O_7$ was obtained. What is the per cent of arsenic in the ore?

In the table (p. 791) we seek as under the heading "Sought" and $Mg_2As_2O_7$ under the heading "Found," and we find on the same line that the chemical factor is 0.4827. Finally, in the fourth column we find that the logarithm of this number multiplied by 100 is 1.6837. The computation is as follows:

log factor × 100	1.6837
log 0.4761	9.6777 − 10
colog 0.5	0.3010
	1.6624 log of 45.96

The ore contains 45.96 per cent of arsenic.

If the weight of ore had been 0.4827 g (a so-called *factor* weight) the percentage of arsenic would have been found by multiplying the weight of precipitate by 100.

This table of factors is convenient, but every chemist should know how to compute any factor. As this often causes trouble for beginners, the method of computing the factors will be discussed.

Computing the Factor. — The symbol AgCl shows that one atomic weight of silver, 107.88, is present in 1 molecular weight of silver chloride, 143.34. This ratio of weights is independent of the unit of weight used and is just as true of tons, pounds, ounces or grains as it is of grams. Using the conception of the gram-molecular weight, the formula shows that 107.88 g of silver are present in 143.34 g of silver chloride. If 143.34 g of silver chloride contain 107.88 g of silver, 1 g of silver chloride will contain $\frac{107.88}{143.34} = 0.7526$ g silver. In other words, the chemical

factor for silver in silver chloride is found by dividing the atomic weight of silver by the molecular weight of silver chloride. Using symbols, the chemical factor in this case is $\frac{Ag}{AgCl}$. It represents the ratio of *what is sought* to *what has been found.*

In the case of the arsenic analysis referred to above, the symbol for magnesium pyroarsenate, $Mg_2As_2O_7$, shows that 2 atoms of arsenic are present in the molecule. The chemical factor is $\frac{2\ As}{Mg_2As_2O_7} = \frac{149.9}{310.6} = 0.4827.$

As a still more complicated case, assume that a sample of magnetite is analyzed in such a way that all the iron is converted into Fe_2O_3 and it is desired to know the weight of Fe_3O_4 originally present. The chemical factor for converting a weight of Fe_2O_3 into the equivalent weight of Fe_3O_4 is $\frac{2\ Fe_3O_4}{3\ Fe_2O_3} = \frac{463.1}{479.1} = 0.9666.$

The concept of the *chemical factor* may be applied to any chemical equation as well as to any precipitate. The following equation represents the reaction between ferrous ions and dichromate ions:

$$6\ Fe^{++} + Cr_2O_7^{--} + 14\ H^+ \rightarrow 6\ Fe^{+++} + 2\ Cr^{+++} + 7\ H_2O$$

On the basis of this equation we can compute the weight of ferrous ammonium sulfate which will react with a given weight of potassium dichromate. The chemical factor is

$$\frac{6\,[FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6\ H_2O]}{K_2Cr_2O_7} = \frac{6 \times 392.1}{294.2} = 7.998$$

If the weight of dichromate is multiplied by this factor the product will be the equivalent of ferrous ammonium sulfate. If a weight of ferrous ammonium sulfate is divided by 7.998, the quotient is the equivalent weight of dichromate.

It is possible to arrive at the same result by a slightly different method of reasoning and this other method is more like the method used in volumetric computations. If the weight of ferrous ammonium sulfate, p, is divided by the molecular weight of ferrous ammonium sulfate, the quotient represents the number of moles of ferrous ammonium sulfate present. The equation, however, shows that one-sixth as many moles of dichromate are required so that by dividing by six and multiplying by the molecular weight of dichromate the weight of dichromate is obtained. In each case the computation may be expressed as follows:

$$\frac{p \times K_2Cr_2O_7}{FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O \times 6} = \text{weight of dichromate}$$

The fraction $\frac{K_2Cr_2O_7}{6FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O}$ represents the weight of dichromate which corresponds to 1 g of ferrous ammonium sulfate, the fraction

$$\frac{\quad}{FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O}$$

represents the number of moles of ferrous ammonium sulfate present.

It is evident from the foregoing discussion that ordinary chemical arithmetic is really very simple. Formerly the so-called "rule of three" was used more in elementary texts on arithmetic than it is today. In Germany it is still used more than in the United States. Most text-books on analytical chemistry have been influenced by German practice and beginners in chemistry have been taught to use proportions in chemical arithmetic instead of reasoning out unit values as they have been taught before studying chemistry. In the above discussion not

a single proportion has been written out to be solved mechanically by the rule that "the product of the means is equal to the product of the extremes."

Computations of Volumetric Analysis.

1. *Relative Strength of Solutions.*

(*a*) If a milliliters of solution A = b milliliters of solution B, then

1 ml of solution $A = \frac{b}{a}$ milliliters solution B; 1 ml of $B = \frac{a}{b}$ milliliters of A.

(*b*) If solution A is N-normal, then solution B is $\frac{a}{b} \times N$-normal.

(*c*) If solution A is N-normal and solution B is M-normal, then 1 ml of $A = N/M$ milliliters of B; 1 ml of $B = M/N$ milliliters of A.

2. *Normal Strength or Normality.*

The *normal strength* gives the number of milli-equivalents contained in 1 ml of solution. Thus, 1 ml of a normal solution contains 1 milli-equivalent in each milliliter.

(*a*) To find the normality, divide the value of 1 ml in terms of any pure substance by the milli-equivalent of that substance. Thus, if ml represents the number of milliliters of solution that contain or are equivalent to g grams of a pure substance (of which the milli-equivalent is e), then the normality, N, is $\frac{g}{ml \times e} = N$.

(*b*) If N be the normality, and e the milli-equivalent, then 1 ml of the solution $= e \times N$ grams of the substance in question.

The milli-equivalent may be part of the molecule: thus

1 ml of 0.3 N acid $= 0.3 \times 0.031$ g of Na_2O.

3. *General Method of Finding the Percentage by Weight.*

Let ml represent the net volume of reagent required, N the normality of the reagent, s the weight of substance taken, and e the milli-equivalent weight of the constituent whose percentage is required.

Then $\frac{ml \times N \times e \times 100}{s}$ = per cent.

Note that if $s = N \cdot e \cdot 100$, then ml = per cent.

4. *Equivalent Weights.*

(*a*) Acids. Let M = molecular weight, MO = methyl orange, P = phenolphthalein. The first three acids may be titrated with either indicator.

Acid	*Equivalent*
HCl	M
HNO_3	M
H_2SO_4	M/2
$HC_2H_3O_2$	M (With P)
$H_2C_4H_4O_6$	M/2 (With P)
H_2CO_3	M (With P)
$KHC_4H_4O_6$	M (With P)

$H_2C_2O_4 \cdot 2H_2O$	M/2 (With P)
KHC_2O_4	M (With P)
$KHC_2O_4 \cdot H_2C_2O_4 \cdot 2H_2O$	M/3 (With P)
H_3PO_4	M (With MO)
H_3PO_4	M/2 (With P)
H_3BO_3	M (With P and glycerol, not acid to MO)

(*b*)

Bases	*Equivalent*
KOH	M
NaOH	M
NH_4OH	M (With MO)
$Ba(OH)_2$	M/2

(*c*) SALTS OF WEAK ACIDS

Salts of carbonic and boric acids may be titrated with methyl orange as if the free base were present. With phenolphthalein the end-point is reached when the carbonate is completely changed to bicarbonate. Thus Na_2CO_3 titrates as if it were 2 NaOH with methyl orange but reacts with only one (1) equivalent of acid if phenolphthalein is used in the cold.

(*d*) OXIDIZING AGENTS:

Substance	*Reduction Change*	*Equivalent*
	Each Cr loses 3 charges	M/6
$KMnO_4$	Mn^{+II}	M/5
$KMnO_4$	MnO_2	M/3
MnO_2		M/2
$KBrO_3$ or KIO_3	(Br or I)$^{+V}$ to (Br or I)$^{-I}$	M/6
Free Cl, Br, I	To (Cl, Br, or I)$^{-I}$	At. Wt.
Cu^{++} (Iodide method)	To Cu^{+}	At. Wt.
Na_2O_2	$O^{\pm}$ to $O^{=}$	M/2

(*e*) REDUCING AGENTS:

Substance	*Oxidation Change*	*Equivalent*
H_2S	$S^{=}$ to S^{0}	M/2
$SnCl_2$	Sn^{++} to Sn^{+}	M/2
HI	I^{-} to I^{0}	M
Zn	Zn^{0} to	M/2
Fe	Fe^{0} to Fe^{++}	At. Wt.
Fe (After solution in acid)		At. Wt.
Fe (Any ferrous salt containing 1 Fe)	Fe^{++} to	M
H_2O_2 (With $KMnO_4$)	$O^{\pm}$ to O^{++}	M/2
$K_4Fe(CN)_6$	To $[Fe(CN)_6]^{\equiv}$	M
$H_2C_2O_4 \cdot H_2O$ or KHC_2O_4 or	To 2 CO_2	M/2
$KHC_2O_4 \cdot H_2C_2O_4 \cdot 2H_2O$	To 4 CO_2	M/4
	To $\frac{1}{2}$ $Na_2S_4O_6$	M
As_2O_3	To $2AsO_3^{\equiv}$ or $2AsO_2^{-}$	M/4

5. *Equivalent weight depends on the reaction.*

Considered as a salt (that is, as if it were a precipitant) the equivalent weight of $KMnO_4 = M$. A solution of $KMnO_4$ which is normal as a salt would be 5 N in a reaction with a ferrous salt whereby the Mn loses 5 valence charges, and would be 3 N in a reaction whereby the $KMnO_4$ is only reduced to MnO_2.

Similarly the equivalent weight of potassium binoxalate, KHC_2O_4, or of potassium tetroxalate $KHC_2O_4 \cdot H_2C_2O_4 \cdot 2H_2O$, depends upon the replaceable hydrogen when considered as an acid, but as reducing agents the oxalate content alone is to be considered. A solution of tetroxalate which is normal as an acid is four-thirds normal as a reducing agent. Arsenic acid is like phosphoric acid as an acid, but in the reaction with hydriodic acid the As is reduced from the quinquevalent to the trivalent state (cf. pp. 473–477).

CHEMICAL FACTORS*

Sought	Found	Factor	Log
Ag	AgBr	0.5744	9.7593
	AgCl	0.7526	9.8766
	AgCN	0.8058	9.9062
	AgI	0.4595	9.6622
	$AgNO_3$	0.6350	9.8028
	Ag_2O	0.9310	9.9689
	Ag_2S	0.8706	9.9398
	Ag_3PO_4	0.7731	9.8882
	$Ag_4P_2O_7$	0.7125	9.8528
Ag_2O	AgCl	0.8084	9.9076
Al	Al_2O_3	0.5291	9.7236
	$AlPO_4$	0.2210	9.3446
Al_2O_3	$AlPO_4$	0.4178	9.6210
AlF_3	CaF_2	0.7170	9.8555
$AlCl_3$	Al_2O_3	2.616	0.4177
$Al_2(SO_4)_3$	Al_2O_3	3.356	0.5258
$Al_2(SO_4)_3.18H_2O$	Al_2O_3	6.537	0.8154
As	As_2O_3	0.7575	9.8794
	As_2O_5	0.6521	9.8143
	As_2S_3	0.6091	9.7847
	As_2S_5	0.4832	9.6841
	I_2	0.2953	9.4703
	$Mg_2As_2O_7$	0.4827	9.6837
	$Mg_2P_2O_7$	0.6731	9.8281
	$(NH_4MgAsO_4)_2H_2O$	0.3939	9.5953
As_2O_3	As_2O_5	0.8609	9.9349
	As_2S_3	0.8041	9.9053
	As_2S_5	0.6378	9.8047
	$2I_2$	0.3900	9.5909
	$Mg_2As_2O_7$	0.6372	9.8043
	$Mg_2P_2O_7$	0.8887	9.9487
	$(NH_4MgAsO_4)_2H_2O$	0.5199	9.7160
AsO_3	As_2S_3	0.9992	9.9996
	As_2S_5	0.7926	9.8991
	$Mg_2As_2O_7$	0.7919	9.8987

Sought	Found	Factor	Log
AsO_3	$Mg_2P_2O_7$	1.104	0.0430
	$(NH_4MgAsO_4)_2H_2O$	0.6460	9.8103
As_2O_5	As_2S_3	0.9341	9.9704
	As_2S_5	0.7410	1.8698
	$2I_2$	0.4529	9.6560
	$Mg_2As_2O_7$	0.7403	1.8694
	$Mg_2P_2O_7$	1.032	0.0138
	$(NH_4MgAsO_4)_2H_2O$	0.6040	9.7810
AsO_4	As_2S_3	1.129	0.0528
	As_2S_5	0.8957	9.9522
	I_2	0.5473	9.7383
	$Mg_2As_2O_7$	0.8949	9.9518
	$Mg_2P_2O_7$	1.2477	0.0962
	$(NH_4MgAsO_4)_2.H_2O$	0.7301	9.8634
Au	$AuCl_3$	0.6496	9.8126
	$HAuCl_4.4H_2O$	0.4785	9.6799
	$KAu(CN)_4.H_2O$	0.5500	9.7403
B	B_2O_3	0.3107	9.4924
	KBF_4	0.08593	8.9342
	H_3BO_3	0.1750	9.2430
	$Na_2B_4O_7.10H_2O$	0.1135	9.0549
B_2O_3	KBF_4	0.2766	9.4418
	H_3BO_3	0.5630	9.7505
	$Na_2B_4O_7.10H_2O$	0.3652	9.5625
BO_2	B_2O_3	1.229	0.0898
BO_3	B_2O_3	1.689	0.2277
B_4O_7	B_2O_3	1.115	0.0472
Ba	$BaCl_2.2H_2O$	0.5621	9.7498
	$BaCO_3$	0.6961	9.8426
	$BaCrO_4$	0.5422	9.7341
	$BaSO_4$	0.5885	9.7697
	$BaSiF_6$	0.4916	9.6916
BaO	$BaCO_3$	0.7771	9.8905
	$BaCrO_4$	0.6053	9.7820
	$BaSO_4$	0.6570	9.8176
	$BaSiF_6$	0.5489	9.7395

* The use of the table will be illustrated by two examples. (1) What weight of silver corresponds to p grams of silver bromide? Look up Ag in the column "Sought" and AgBr in the column "Found." For computation with a slide rule, use column 3, $p \times 0.5744$ = weight of Ag. With logarithms, log p + 9.7592 = log weight of Ag. (2) What weight of silver bromide corresponds to q grams of silver? Use the same factor as before, but *divide* by it or *subtract* the logarithm.

Strictly speaking, the logarithm in the above case is not 9.7592 but 9.7592 − 10 or $\bar{1}.7592$, in which the characteristic is a negative number and the mantissa a positive fraction. It is a little easier to use the first expression and in chemical computations it is not necessary to write out the −10 each time because there is never any doubt whether a characteristic of 7, 8, or 9 represents a very large number or a number less than unity.

In computing the weight of silver bromide instead of subtracting the logarithm 9.7592 it is more convenient to add the co-logarithm 0.2407 which is obtained quickly by subtracting each digit of 9.7592 from 9 except the last one which is subtracted from 10. It gives the logarithm of $\frac{1}{0.5744}$ = 0.2408.

CHEMICAL FACTORS — *Continued*

Sought	Found	Factor	Log
BaO_2	Ba.....	1.233	0.0909
	$BaCrO_4$	0.6685	9.8251
	$BaSO_4$..	0.7256	9.8607
$BaCO_3$	$BaSO_4$.	0.8458	9.9272
$BaCl_2.2H_2O$	$BaSO_4$.	1.047	0.0198
$BaCrO_4$	$BaSO_4$.	1.085	0.0356
BaF_2	$BaSiF_6$	0.6276	9.7977
$Ba(NO_3)_2$	$BaSO_4$.	1.120	0.0491
$Ba_3(PO_4)_2$	$BaSO_4$.	0.8599	9.9345
BaS	$BaSO_4$.	0.7258	9.8608
Be	BeO..........	0.3605	9.5569
BeO	$BeCl_2$.........	0.3130	.4956
BeO	$BeSO_4.4H_2O$..	0.1412	9.1500
Bi	Bi_2O_3...	0.8970	9.9528
	$BiOCl$..	0.8024	9.9044
	$BiPO_4$.	0.6874	9.8372
	Bi_2S_3...	0.8129	9.9101
	$BiAsO_4$.	0.6006	9.7786
Bi_2O_3	Bi.............	1.115	0.0472
	$BiOCl$.........	0.8946	9.9516
	$BiPO_4$.........	0.7663	9.8844
	Bi_2S_3..........	0.9063	0.9573
	$BiAsO_4$........	0.6696	9.8258
	$BiONO_3$........	0.8118	9.9095
	$Bi(NO_3)_3.5H_2O$	0.4803	9.6815
Br	Ag...	0.7408	9.8697
	$AgBr$.	0.4256	9.6290
	$AgCl$.	0.5576	9.7463
	HBr..	0.9874	9.9945
BrO_3	Ag...	1.186	0.0740
	$AgBr$.	0.6812	9.8332
Br_2O_5	Ag...	1.111	0.0459
	$AgBr$.	0.6386	9.8052
	CO_2...	0.2727	9.4357
	$BaCO_3$	0.0608	8.7839
CO_2	$BaCO_3$......	0.2229	9.3482
	BaO........	0.2869	9.4577
	$Ba(HCO_3)_2$.	0.3395	9.5309
	$CaCO_3$.....	0.4396	9.6430
	$Ca(HCO_3)_2$.	0.5431	9.7349
	CaO........	0.7846	
	CO_3........	0.7333	9.8653
	Cs_2CO_3.....	0.1351	9.1307
	$FeCO_3$......	0.3798	9.5796
	$Fe(HCO_3)_2$.	0.4948	9.6944
	K_2CO_3......	0.3184	9.5029
	$KHCO_3$....	0.4395	9.6430
	$_2CO_3$	0.5956	9.7749
	$LiHCO_3$.	0.6476	9.8113

Sought	Found	Factor
CO_2	$MgCO_3$......	0.5218
	$Mg(HCO_3)_2$.	0.6014
	MgO........	1.091
	$MnCO_3$......	0.3828
	$Mn(HCO_3)_2$.	0.4973
	Na_2CO_3......	0.4151
	$NaHCO_3$.....	0.5238
		0.7098
	$(NH_4)_2CO_3$.	0.4580
	$PbCO_3$.......	0.1647
	Rb_2CO_3......	0.1907
	$Rb(HCO_3)$.	0.3005
	$SrCO_3$.......	0.2980
	$Sr(HCO_3)_2$.	0.4198
	SrO.........	0.4251
	$ZnCO_3$......	0.3509
CO_3	CO_2.	1.364
Ca	$CaC_2O_4.H_2O$.	0.2743
	CaC_2O_4......	0.3129
	$CaCl_2$.......	0.3612
	$CaCO_3$......	0.4005
	CaF_2........	0.5133
	CaO.........	0.7146
	$CaSO_4$.......	0.2944
	CO_2.........	0.9109
CaO	$CaC_2O_4.H_2O$..	0.3838
	CaC_2O_4.......	0.4378
	$CaCO_3$........	0.5603
	CaF_2.........	0.7182
	$Ca(HCO_3)_2$...	0.3459
	$Ca(H_2PO_4)_2.H_2O$	0.2224
	$Ca_2P_2O_7$.....	0.4411
	$Ca(HSO_3)_2$...	0.2773
	$Ca_3(PO_4)_2$....	0.5421
	$CaSO_3$.......	0.4667
	$CaSO_4$.......	0.4120
	$CaSO_4.2H_2O$.	0.3257
	CO_2.........	1.274
$Ca_3(PO_4)_2$	$Mg_2P_2O_7$.	1.393
CaS	$BaSO_4$...	0.3091
$CaSO_4$	$BaSO_4$...	0.5832
$CaSO_4.2H_2O$	CaO	3.071
CaF_2	$CaSO_4$	0.5735
Cb	Cb_2O_5	0.6999
Cd	CdO...	0.8754
	CdS...	0.7780
	$CdSO_4$.	0.5392
CdO	CdS...	0.8888
	Cd....	1.142
	$CdSO_4$.	0.6159

CHEMICAL FACTORS — *Continued*

Sought	Found	Factor	Log
CdS	Cd	1.2853	0.1090
	CdO	1.1252	0.0512
	$CdSO_4$	0.6930	9.8407
Ce	$Ce(NO_3)_4$	0.3610	
	Ce_2O_3	0.8538	9.9313
	CeO_2	0.8141	9.9107
	$Ce(SO_4)_3$	0.4930	9.6929
Ce_2O_3	CeO_2	0.9536	9.9794
Cl	Ag	0.3287	9.5168
	AgCl	0.2474	9.3934
	$AgNO_3$	0.2087	9.3195
	HCl	0.9724	9.9879
	I	0.2794	9.4462
	KCl	0.4756	9.6772
	MnO_2	0.8158	9.9116
	NaCl	0.6066	9.7829
	NH_4Cl	0.6628	9.8214
	RbCl	0.2933	9.4673
ClO_3	AgCl	0.5823	9.7651
	KCl	1.119	0.0490
	NaCl	1.428	0.1546
ClO_4	AgCl	0.6939	0.8413
	KCl	1.334	0.1251
	NaCl	1.701	0.2308
CN	AgCN	0.1943	9.2884
	Ag	0.2411	9.3822
	KCN	0.3999	9.6020
	NaCN	0.5313	9.7253
	HCN	0.9627	9.9835
CNS	AgCNS	0.3500	9.5440
	$Cu_2(CNS)_2$	0.4774	9.6789
	$BaSO_4$	0.2488	9.3959
	KCNS	0.5974	9.7765
	NH_4CNS	0.7632	9.8825
Co	$Co(NO_3)_2.6H_2O$	0.2026	9.3066
	$K_3Co(NO_2)_6$	0.1304	9.1152
	CoO	0.7866	9.8957
	Co_3O_4	0.7344	9.8659
	$CoSO_4$	0.3804	9.5802
	$CoSO_4.7H_2O$	0.2097	9.3216
CoO	Co	1.2713	0.1043
	$Co(NO_3)_2.6H_2O$	0.2575	9.4109
	$K_3Co(NO_2)_6$	0.1657	9.2194
	Co_3O_4	0.9336	9.9702
	$CoSO_4$	0.4836	9.6844
	$CoSO_4.7H_2O$	0.2667	9.4259
Cr	$BaCrO_4$	0.2052	9.3125
	Cr_2O_3	0.6842	9.8352

Sought	Found	Factor	Log
Cr	$PbCrO_4$	0.1609	9.2067
	$K_2Cr_2O_7$	0.3535	9.5484
	K_2CrO_4	0.2678	9.4278
Cr_2O_3	$BaCrO_4$	0.3000	9.4771
	$PbCrO_4$	0.2352	9.3715
	CrO_3	0.7602	9.8809
CrO_3	$BaCrO_4$	0.3947	9.5963
	Cr_2O_3	1.3158	0.1192
	$PbCrO_4$	0.3095	9.4907
	K_2CrO_4	0.5150	9.7118
	$K_2Cr_2O_7$	0.6800	9.8325
CrO_4	$BaCrO_4$	0.4578	9.6607
	r_2O_3	1.5263	0.1837
	$PbCrO_4$	0.3589	9.5550
Cs	sCl	0.7893	9.8973
	Cs_2O	0.9432	9.9746
	C	0.8157	9.9116
	s_2SO_4	0.7344	9.8659
		0.3945	9.5960
Cs_2O	sCl	0.8370	0.9227
		0.8650	9.9370
		0.7786	9.8913
		0.4182	9.6214
Cu		0.8882	9.9485
		0.7989	9.9025
	2	0.7986	9.9023
	$u_2(CNS)_2$	0.5226	9.7181
	uSO_4	0.3982	9.6001
	$uSO_4.5H_2O$	0.2546	9.4058
CuO		1.252	0.0975
		1.113	0.0463
		0.9996	9.9998
		0.6541	9.8156
		0.4985	9.6976
	$uSO_4.5H_2O$	0.3186	9.5032
Er_2O_3		1.145	0.0589
Er		0.8732	9.9411
	$BaSiF_6$	0.4080	9.6107
	aF_2	0.4866	9.6872
	$CaSO_4$	0.2791	9.4457
	HF	0.9496	9.9776
	H_2SiF_6	0.7913	9.8983
	K_2SiF_6	0.5176	9.7140
	NaF	0.4524	9.6555
	SiF_4	0.7302	9.8634
Fe	Fe_2O_3	0.6994	9.8447
	$FeCl_2$	0.4405	9.6440
	$FeCl_3.6H_2O$	0.2066	9.3152

CHEMICAL FACTORS — *Continued*

Sought	Found	Factor	Log
Fe	$Fe(HCO_3)_2$	0.3140	9.4969
	FeO	0.7773	9.8906
	Fe_3O_4	0.7236	9.8595
	$FePO_4$	0.3701	9.5683
	FeS	0.6352	9.8029
	$FeSO_4$	0.3676	9.5654
	$FeSO_4.7H_2O$	0.2009	9.3029
	$FeSO_4(NH_4)_2SO_4.6H_2O$	0.1424	9.1536
FeO	Fe	1.287	0.1094
	$FeCO_3$	0.6202	9.7925
	$Fe(HCO_3)_2$	0.4039	9.6063
	Fe_2O_3	0.8998	9.9542
	$FePO_4$	0.4761	9.6777
	FeS	0.8172	9.9123
	$FeSO_4$	0.4729	9.6747
	$FeSO_4.7H_2O$	0.2584	9.4123
	$FeSO_4(NH_4)_2SO_4.6H_2O$	0.1832	9.2630
Fe_2O_3	Fe	1.430	0.1553
	$FeCl_3$	0.4922	9.6922
	$FeCO_3$	0.6892	9.8383
	Fe_3O_4	1.035	0.0149
	$FePO_4$	0.5292	9.7237
	FeS	0.9082	9.9582
	FeS_2	0.6655	9.8231
	$Fe_2(SO_4)_3$	0.3993	9.6013
	$(NH_4)_2SO_4.Fe_2(SO_4)_3.24H_2O$	0.1656	9.2190
FeS_2	$BaSO_4$	0.2570	9.4099
H	H_2O	0.1119	9.0488
H_3BO_3	B_2O_3	1.776	0.2495
HBr	Ag	0.7501	9.8751
	$AgBr$	0.4309	9.6344
HCl	Ag	0.3380	9.5290
	$AgCl$	0.2544	9.4056
	$CaCO_3$	0.7288	9.8626
	KCl	0.4891	9.6894
	K_2O	0.7743	9.8889
	$NaCl$	0.6239	9.7951
	Na_2O	1.176	0.0705
	NH_4Cl	0.6817	9.8335
	$SnCl_4$	0.5600	9.7480
	Na_2CO_3 methyl orange	0.6881	9.8377
	$Na_2C_2O_4$ standardization	0.5442	9.7358
HF	$BaSiF_6$	0.4296	9.6331
	CaF_2	0.5126	9.7098
	$CaSO_4$	0.2939	9.4682

Sought	Found	Factor	Log
HF	F	1.053	0.0224
	K_2SiF_6	0.5449	9.7363
HI	Ag	1.186	0.0742
	AgI	0.5448	9.7362
	Pd	2.398	0.3799
	PdI_2	0.7097	9.8510
HNO_2	$AgNO_2$	0.3055	9.4850
	NO	1.567	0.1950
HNO_3	KNO_3	0.6233	9.7947
	N	4.498	0.6530
	$NaNO_3$	0.7413	9.8700
	NH_3	3.701	0.5683
	NH_4Cl	1.178	0.0711
	$(NH_4)_2PtCl_6$	0.2838	9.4530
	NO	2.100	0.3222
	N_2O_3	1.658	0.2196
	N_2O_4	1.370	0.1367
	N_2O_5	1.167	0.0671
	$C_{20}H_{16}N_4HNO_3$	0.1680	9.2252
	Pt	0.6457	9.8100
H_3PO_4	HPO_3	1.225	0.0881
	$H_4P_2O_7$	1.101	0.0457
	$Mg_2P_2O_7$	0.8806	9.9448
	P	3.159	0.4995
	P_2O_5	1.380	0.1399
$H_2PtCl_6.6H_2O$	Pt	2.654	0.4239
H_2S	$BaSO_4$	0.1460	9.1644
	CdS	0.2360	9.3729
	FeS	0.3877	9.5885
	S	1.063	0.0265
H_2SeO_3	Se	1.632	0.2126
H_2SiF_6	$BaSiF_6$	0.5157	9.7124
	$3CaF_2$	0.6149	9.7888
	F	1.264	0.1018
	$2HF$	3.601	0.5564
	$6HF$	1.200	0.0792
	K_2SiF_6	0.6541	9.8157
	SiF_4	1.384	0.1412
H_2SO_4	$Al_2(SO_4)_3$	0.8594	9.9342
	$Ba(OH)_2$	0.5719	9.7574
	$BaSO_4$	0.4200	9.6232
	$K_2Al_2(SO_4)_4.24H_2O$	0.4132	9.6162
	K_2O	1.041	0.0174
	KOH	0.8736	9.9413
	K_2SO_4	0.5625	9.7501
	Na_2CO_3	0.9252	9.9662
	$Na_2C_2O_4$	0.7318	9.8642

CHEMICAL FACTORS — *Continued*

Sought	Found	Factor	Log
H_2SO_4	$(NH_4)_2SO_4$....	0.7418	9.8703
Hg	Hg_2Cl_2	0.8498	9.9293
	$HgCl_2$.	0.7388	9.8686
	HgO...	0.9261	9.9666
	HgS...	0.8620	9.9355
HCNS	AgCNS....	0.3560	9.5515
	$Cu_2(CNS)_2$	0.4857	9.6864
	$BaSO_4$.....	0.2531	9.4033
Hg_2Cl_2	$SnCl_2$	2.486	0.3956
$HgCl_2$	Hg_2Cl_2.	1.150	0.0607
	HgS...	1.167	0.0671
HgO	Hg_2Cl_2	0.9176	9.9627
HgS	$Hg(CN)_2$.	0.9210	9.9643
	$HgNO_3$...	0.8860	9.9474
	$Hg(NO_3)_2$	0.7167	9.8554
	Hg_2O.....	1.115	0.0474
	HgO......	1.074	0.0311
	$HgSO_4$....	0.7843	9.8945
	Ag...........	1.177.	0.0706
	AgI..........	0.5406	9.7328
	KI...........	0.7645	9.8834
	Pd...........	2.379	0.3764
	PdI_2..........	0.7041	9.8476
	$Na_2S_2O_3.5H_2O$.	0.5113	9.7087
	AgCl.........	0.8855	9.9472
In	In_2O_3	0.8271	9.9176
	In_2S_3.	0.7047	9.8480
Ir	Ir_2O_3	0.8894	9.9491
K	KCl.....	0.5244	9.7197
	K_2O.....	0.8300	9.9191
	K_2SO_4...	0.4487	9.6520
	$KClO_4$...	0.2822	9.4505
	K_2PtCl_6.	0.1609	9.2064
	Pt.......	0.4006	9.6027
KCl	Ag......	0.6911	9.8396
	AgCl....	0.5202	.7162
	K_2SO_4...	.8557	.9323
	$KClO_4$...	.5381	9.7309
	K_2PtCl_6.	.3067	9.4868
	Pt.......	.7638	
K_2O	KCl.....	.6317	.8005
	K_2SO_4...	.5405	.7328
	$KClO_4$...	.3399	.5314
	K_2PtCl_6.	.1938	.2873
	Pt.......	.4826	.6836
$KClO_3$	AgCl...........	0.8550	9.9320
	KCl............	1.6438	0.2158
$KClO_4$	AgCl...........	0.9667	9.9853
	KCl............	1.858	0.2691
KCN	AgCN.........	0.4863	9.6869
	$AgNO_3$ (Liebig method).....	0.7665	9.8845
	AgCl..........	0.4542	9.6573
K_2SO_4	K......	2.229	0.3481
	KCl....	1.169	0.0679
	K_2O....	1.850	0.2672
	K_2PtCl_6.	0.3585	9.5545
	SO_3.....	2.177	0.3379
	$BaSO_4$...	0.7465	9.8731
La	La_2O_3...........	0.8527	9.9308
Li	LiCl...	0.1637	9.2140
	Li_2O...	0.4643	9.6669
	Li_3PO_4.	0.1797	9.2545
	Li_2SO_4.	0.1262	9.1012
Li_2O	LiCl..	0.3524	9.5470
	Li_2SO_4	0.2718	9.4342
	Li_3PO	0.3870	9.5877
Mg	MgO...........	0.6032	9.7804
	$MgSO_4$..........	0.2020	9.3054
	$Mg_2P_2O_7$........	0.2184	9.3392
	$MgSO_4$.........	0.2020	9.3054
	H_2O.........	0.09907	8.9960
	$O_4.H_2O$	0.1565	9.1945
MgO		0.3349	9.5249
	$Mg_2P_2O_7$	0.3621	9.5588
	$MgCO_3$....	0.4782	9.6796
	$MgNH_4PO_4$ 6H_2O.	0.1642	9.2155
	$MgNH_4PO_4.H_2O$	0.2595	9.4141
Mn	$MnCO_3$.	0.4779	9.6793
	MnO...	0.7744	9.8889
	3.........	0.6959	9.8426
	Mn_3O_4.........	0.7203	9.8575
	$MnSO_4$.........	0.3638	9.5608
	$Mn_2P_2O_7$........	0.3869	9.5876
		0.6314	9.8003
MnO	$MnCO_3$.........	0.6172	9.7904
	Mn_3O_4.........	0.9301	9.9685
	$MnSO_4$.	0.4697	9.6719
	MnS.....	0.8153	9.9113
	$Mn_2P_2O_7$.	0.4998	

CHEMICAL FACTORS — *Continued*

Sought	Found	Factor	Log
Mo	MoO_3	0.6667	9.8239
	MoS_3	0.4995	9.6985
	MoS_2	0.5996	9.7779
	$PbMoO_4$	0.2615	9.4174
MoO_3	MoS_3	0.7492	9.8746
	$(NH_4)_2MoO_4$	0.7344	9.8659
	$(NH_4)_3PO_4(MoO_3)_{12}$	0.9205	9.9640
	$PbMoO_4$	0.3923	9.5936
N	HNO_3	0.2223	9.3470
	NO_2	0.3045	9.4835
	N_2O_3	0.3686	9.5665
	N_2O_4	0.3045	9.4835
	N_2O_5	0.2594	9.4140
	$NaNO_3$	0.1648	9.2169
	NH_3	0.8225	9.9151
	Pt	0.1435	9.1570
	NH_4Cl	0.2619	9.4181
Na	NaCl	0.3934	9.5949
	Na_2SO_4	0.3238	9.5103
	NaBr	0.2235	9.3493
	Na_2CO_3	0.4340	9.6375
	NaF	0.5476	9.7385
	$NaHCO_3$	0.2738	9.4374
	NaI	0.1534	9.1858
	Na_2O	0.7419	9.8704
	NaOH	0.5750	9.7597
	Na_2SO_4	0.3238	9.5103
$Na_2B_4O_7$	B_2O_3	1.443	0.1593
	H_3BO_3	0.8142	9.9107
$_2B_4$ H_2O	B_2O_3	2.738	0.4375
	H_3BO_3	1.540	0.1872
	KBF	0.7577	9.8795
NaBr	Ag	0.9539	9.9795
	AgBr	0.5480	9.7388
NaCl	Ag	0.5418	9.7338
	AgCl	0.4078	9.6105
	$AgNO_3$	0.3441	9.5367
	Na_2O	1.886	0.2756
NaF	CaF_2	1.076	0.0317
Na_2HAsO_3		1.095	0.0395
		0.6697	9.8259
Na_2HAsO_4		1.198	0.0785
		0.7328	9.8650
$NaHCO_3$	CO_2	1.909	0.2808
$NaHCO_3$	$KHC_4H_4O_6$	0.4465	9.6498
Na_2O	NaCl	0.5303	9.7245
	Na_2SO_4	0.4364	9.6399
	Na_2CO_3	0.5849	9.7671
	$NaHCO_3$	0.3690	9.5670
	4	0.4365	9.6400
	NaH_2PO_4	0.2582	9.4119
	$Na_2H_2P_2O_7$	0.2792	9.4459
	$NaHSO_3$	0.2979	9.4741
	$NaNO_3$	0.3647	9.5619
	NaOH	0.7748	9.8891
	Na_2SO_4	0.4364	9.6399
Na_2SO_3	$BaSO_4$	0.5401	9.7325
$Na_2S_2O_3$	$BaSO_4$	0.3387	9.5298
	$Na_2S_2O_3.5H_2O$	0.6371	9.8042
Na_2SO_4	$BaSO_4$	0.6086	9.7843
Nd	Nd_2O_3	0.8572	9.9332
NH_3	HNO_3	0.2704	9.4320
	H_2SO_4	0.3473	9.5407
	N	1.216	0.0849
		0.2468	9.3923
	3	0.2005	9.3021
	NH_4Cl	0.3184	9.5029
	$(NH_4)_2HPO_4$	0.2578	9.4113
	$(NH_4)H_2PO_4$	0.1480	9.1703
	$(NH_4)OH$	0.4860	
	$(NH_4)_2PtCl_6$	0.07670	8.8848
	$(NH_4)_2SO_4$	0.2578	9.4113
	N_2O_5	0.3153	9.4987
	Pt	0.1745	9.2418
NH_4	NH_3	1.059	0.0250
	NH_4Cl	0.3372	9.5279
	$(NH_4)_2PtCl_6$	0.08125	8.9099
	Pt	0.1848	9.2668
NH_4Cl	AgCl	0.3732	9.5719
	NH_3	3.141	0.4971
	(	0.2410	1.3820
	Pt	0.5482	9.7389
$(NH_4)_2SO_4$	$BaSO_4$	0.5661	9.7529
Ni	NiO	0.7858	9.8953
	$NiC_8H_{14}N_4O_4$	0.2032	9.3079
	$NiSO_4$	0.3792	9.5788
	$Ni(NO_3)_2.6H_2O$	0.2018	0.3049
	$Ni_2SO_4.7H_2O$	0.2089	9.3200
NO_3	NO	2.066	0.3152
	NH_3	3.640	0.5612

CHEMICAL FACTORS — *Continued*

Sought	Found	Factor	Log
NO_3	NH_4Cl	1.159	0.0641
	$(NH_4)_2PtCl_6$	0.2793	9.4461
	Pt	0.6354	9.8030
	$C_{20}H_{17}N_5O_3$	0.1653	9.2182
N_2O_5	NO	1.800	0.2552
	NH_3	3.171	0.5012
	NH_4Cl	1.010	0.0041
	$(NH_4)_2PtCl_6$	0.2433	9.3861
	Pt	0.5534	9.7430
	$C_{20}H_{17}N_5O_3$	0.1440	9.1582
NO_2	NO	1.533	0.1856
N_2O_3	NO	1.267	0.1026
Os	OsO_4	0.7489	9.8744
	$Mg_2P_2O_7$	0.2787	9.4452
	$P_2O_5.24MoO_3$	0.0173	8.2368
	$(NH_4)_3PO_4.12MoO_3$	0.0165	8.2184
	P_2O_5	0.4369	9.6404
	$MgNH_4PO_4.H_2O$	0.1996	9.3003
	$MgNH_4PO_4.6H_2O$	0.1262	9.1018
PO_4	$Mg_2P_2O_7$	0.8535	9.9312
	$P_2O_5.24MoO_3$	0.05283	8.7229
	$(NH_4)_3PO_4.12MoO_3$	0.05063	8.7044
P_2O_5	$Mg_2P_2O_7$	0.6379	9.8048
	$P_2O_5.24MoO_3$	0.03947	8.5963
	$(NH_4)_3PO_4.12MoO_3$	0.03785	8.5780
	$MgNH_4PO_4.H_2O$	0.4571	9.6600
	$MgNH_4PO_4.6H_2O$	0.2894	9.4615
Pb	PbO	0.9283	9.9677
	PbO_2	0.8662	9.9376
	PbS	0.8659	9.9375
	$PbSO_4$	0.6831	9.8345
	$PbCrO_4$	0.6410	
	$PbCl_2$	0.7449	9.8721
	$PbMoO_4$	0.5642	9.7515
PbO	PbO_2	0.9331	9.9699
	PbS	0.9328	9.9698
	$PbSO_4$	0.7359	9.8668
	$PbCrO_4$	0.6905	9.8392
	$PbCl_2$	0.8025	9.9044
	$PbCO_3$	0.8353	9.9219
	$Pb(NO_3)_2$	0.6738	9.8285
PbS	$PbSO_4$	0.7889	9.8970
	Pb	1.155	0.0626

Sought	Found	Factor	Log
PbS	PbO	1.072	0.0302
	$BaSO_4$	1.025	0.0109
$PbSO_4$	$BaSO_4$	1.299	0.1137
	($3H_2O$	0.7995	9.9028
	$(PbCO_3)_2.Pb(OH)_2$	1.173	0.0693
Rb	AgCl	0.5961	9.7753
	Cl	2.410	0.3820
	RbCl	0.7067	9.8492
	Rb_2CO_3	0.7402	9.8693
	Rb_2O	0.9144	9.9611
	Rb_2SO_4	0.6403	9.8064
	Rb_2PtCl_6	0.2952	9.4701
Rb_2O	RbCl	0.7729	9.8881
	Rb_2SO_4	0.7001	9.8452
RbCl	Rb_2PtCl_6	0.4178	9.6209
	$BaSO_4$	0.1374	9.1379
	H_2S	0.9408	9.9735
	H_2SO_4	0.3270	9.5145
	FeS	0.3648	.5621
	FeS_2	0.5346	9.7280
	Na_2S	0.4108	9.6136
SO_2	$BaSO_4$	0.2745	9.4385
	S	1.998	0.3007
SO_3		0.3430	9.5353
	$CaSO_4$	0.5881	9.7695
	$_2SO_4$	0.8163	9.9119
	K_2SO_4	0.4595	9.6623
	Na_2SO_4	0.5636	9.7510
SO_4	$BaSO_4$	0.4115	9.6144
Sb	½	0.3648	9.5620
	$SbCl_3$	0.5339	9.7275
	Sb_2O_3	0.8356	9.9220
	Sb_2O_5	0.7528	9.8767
	Sb_2O_4	0.7921	9.8988
	Sb_2S_3	0.7169	9.8555
		0.6030	9.7803
Sb_2O_3	Sb_2O_4	0.9479	9.9768
	Sb_2S_3	0.8580	9.9335
	Sb_2S_5	0.7218	9.8584
SeO_2	Se	1.405	0.1474
SeO_3	Se	1.606	0.2058
Si	SiO_2	0.4672	9.6695
	SiO_3	0.3689	9.5669

CHEMICAL FACTORS — *Concluded*

Sought	Found	Factor	Log
Si	SiO_4	0.3048	9.4840
SiO_3	SiO_2	1.266	0.1025
SiO_4	SiO_2	1.532	0.1854
Sn	SnO_2	0.7877	9.8963
	SnO	0.8812	9.9451
	$SnCl_2$	0.6261	9.7967
	$SnCl_2.2H_2O$	0.5260	9.7210
Sr	SrO	0.8456	9.9272
	$SrCO_3$	0.5936	9.7735
	$SrSO_4$	0.4770	9.6785
	$Sr(NO_3)_2$	0.4140	9.6170
SrO	$SrCO_3$	0.7020	9.8463
	$SrSO_4$	0.5641	9.7514
	$Sr(NO_3)_2$	0.4896	9.6899
Ta	$TaCl_5$	0.5057	9.7039
	Ta_2O_5	0.8194	9.9135
Te	TeO_2	0.7994	9.9027
	TeO_3	0.7265	9.8612
Th	ThO_2	0.8788	9.9439
	$Th(NO_3)_4.6H_2O$	0.3947	9.5962
	$ThCl_4$	0.6207	9.7929
ThO_2	$Th(NO_3)_4.6H_2O$	0.4490	9.6523
Ti	TiO_2	0.5996	9.7778
Tl	TlCl	0.8522	9.9305
Tl	Tl_2CO_3	0.8720	9.9405
	TlI	0.6169	9.7902
	$TlNO_3$	0.7672	9.8849
	Tl_2O	0.9623	9.9833
	Tl_2CrO_4	0.7789	9.8915
	Tl_2SO_4	0.8097	9.9083
	$TlHSO_4$	0.6780	9.8312
Tl_2O	Tl_2PtCl_6	0.5200	9.7161
U	U_3O_8	0.8480	9.9284
	UO_2	0.8815	9.9452
	$(UO_2)_2P_2O_7$	0.6667	9.8240
V	V_2O_5	0.5602	9.7483
	V_2O_4	0.6142	9.7883
W	WO_3	0.7931	9.8993
	$PbWO_4$	0.4435	9.6469
Y	Y_2O_3	0.7875	9.8962
Yb	Yb_2O_3	0.8785	9.9437
Zn	ZnO	0.8034	9.9049
	$ZnNH_4PO_4$	0.3663	9.5639
	$Zn_2P_2O_7$	0.4290	9.6324
	ZnS	0.6710	9.8267
ZnO	ZnS	0.8352	9.9218
	$ZnNH_4PO_4$	0.4561	9.6590
	$Zn_2P_2O_7$	0.5340	9.7275
Zr	ZrO_2	0.7403	9.8694

Natural Numbers	0	1	2	3	4	5	6	7	8	9	Proportional Parts 1	2	3	4	5	6	7	8
10	0000	0043	0086	0128	0170	0212	0253	0294	0334	0374	4	8	12	17	21	25	29	33
11	0414	0453	0492	0531	0569	0607	0645	0682	0719	0755	4	8	11	15	19	23	26	30
12	0792	0828	0864	0899	0934	0969	1004	1038	1072	1106	3	7	10	14	17	21	24	28
13	1139	1173	1206	1239	1271	1303	1335	1367	1399	1430	3	6	10	13	16	19	23	26
14	1461	1492	1523	1553	1584	1614	1644	1673	1703	1732	3	6	9	12	15	18	21	24
15	1761	1790	1818	1847	1875	1903	1931	1959	1987	2014	3	6	8	11	14	17	20	22
16	2041	2068	2095	2122	2148	2175	2201	2227	2253	2279	3	5	8	11	13	16	18	21
17	2304	2330	2355	2380	2405	2430	2455	2480	2504	2529	2	5	7	10	12	15	17	20
18	2553	2577	2601	2625	2648	2672	2695	2718	2742	2765	2	5	7	9	12	14	16	19
19	2788	2810	2833	2856	2878	2900	2923	2945	2967	2989	2	4	7	9	11	13	16	18
20	3010	3032	3054	3075	3096	3118	3139	3160	3181	3201	2	4	6	8	11	13	15	17
21	3222	3243	3263	3284	3304	3324	3345	3365	3385	3404	2	4	6	8	10	12	14	16
22	3424	3444	3464	3483	3502	3522	3541	3560	3579	3598	2	4	6	8	10	12	14	15
23	3617	3636	3655	3674	3692	3711	3729	3747	3766	3784	2	4	6	7	9	11	13	15
24	3802	3820	3838	3856	3874	3892	3909	3927	3945	3962	2	4	5	7	9	11	12	14
25	3979	3997	4014	4031	4048	4065	4082	4099	4116	4133	2	3	5	7	9	10	12	14
26	4150	4166	4183	4200	4216	4232	4249	4265	4281	4298	2	3	5	7	8	10	11	13
27	4314	4330	4346	4362	4378	4393	4409	4425	4440	4456	2	3	5	6	8	9	11	13
28	4472	4487	4502	4518	4533	4548	4564	4579	4594	4609	2	3	5	6	8	9	11	12
29	4624	4639	4654	4669	4683	4698	4713	4728	4742	4757	1	3	4	6	7	9	10	12
30	4771	4786	4800	4814	4829	4843	4857	4871	4886	4900	1	3	4	6	7	9	10	11
31	4914	4928	4942	4955	4969	4983	4997	5011	5024	5038	1	3	4	6	7	8	10	11
32	5051	5065	5079	5092	5105	5119	5132	5145	5159	5172	1	3	4	5	7	8	9	11
33	5185	5198	5211	5224	5237	5250	5263	5276	5289	5302	1	3	4	5	6	8	9	11
34	5315	5328	5340	5353	5366	5378	5391	5403	5416	5428	1	3	4	5	6	8	9	10
35	5441	5453	5465	5478	5490	5502	5514	5527	5539	5551	1	2	4	5	6	7	9	10
36	5563	5575	5587	5599	5611	5623	5635	5647	5658	5670	1	2	4	5	6	7	8	10
37	5682	5694	5705	5717	5729	5740	5752	5763	5775	5786	1	2	3	5	6	7	8	10
38	5798	5809	5821	5832	5843	5855	5866	5877	5888	5899	1	2	3	5	6	7	8	9
39	5911	5922	5933	5944	5955	5966	5977	5988	5999	6010	1	2	3	4	5	7	8	9
40	6021	6031	6042	6053	6064	6075	6085	6096	6107	6117	1	2	3	4	5	6	8	9
41	6128	6138	6149	6160	6170	6180	6191	6201	6212	6222	1	2	3	4	5	6	7	8
42	6232	6243	6253	6263	6274	6284	6294	6304	6314	6325	1	2	3	4	5	6	7	8
43	6335	6345	6355	6365	6375	6385	6395	6405	6415	6425	1	2	3	4	5	6	7	8
44	6435	6444	6454	6464	6474	6484	6493	6503	6513	6522	1	2	3	4	5	6	7	8
45	6532	6542	6551	6561	6571	6580	6590	6599	6609	6618	1	2	3	4	5	6	7	8
46	6628	6637	6646	6656	6665	6675	6684	6693	6702	6712	1	2	3	4	5	6	7	7
47	6721	6730	6739	6749	6758	6767	6776	6785	6794	6803	1	2	3	4	5	5	6	7
48	6812	6821	6830	6839	6848	6857	6866	6875	6884	6893	1	2	3	4	4	5	6	7
49	6902	6911	6920	6928	6937	6946	6955	6964	6972	6981	1	2	3	4	4	5	6	7
50	6990	6998	7007	7016	7024	7033	7042	7050	7059	7067	1	2	3	3	4	5	6	7
51	7076	7084	7093	7101	7110	7118	7126	7135	7143	7152	1	2	3	3	4	5	6	7
52	7160	7168	7177	7185	7193	7202	7210	7218	7226	7235	1	2	2	3	4	5	6	7
53	7243	7251	7259	7267	7275	7284	7292	7300	7308	7316	1	2	2	3	4	5	6	6
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Natural Numbers	0	1	2	3	4	5	6	7	8	9	Proport[illegible] 1	2	3	4	5	6	7	8	9
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57	7559	7566	7574	7582	7589	7597	7604	7612	7619	7627	1	2	2	3	4	5	5	6	7
58	7634	7642	7649	7657	7664	[illegible]72	7679	7686	7694	7701	1	1	2	3	4	4	5	6	7
59	7709	7716	7723	7731	7738	7[illegible]45	7752	7760	7767	7774	1	1	2	3	4	4	5	6	7
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61	7853	7860	7868	7875	7882	7889	7896	7903	7910	7917	1	1	2	3	4	4	5	6	6
62	7924	7931	7938	7945	7952	7959	7966	7973	7980	7987	1	1	2	3	3	4	5	6	6
63	7993	8000	8007	8014	8021	8028	8035	8041	8048	8055	1	1	2	3	3	4	5	5	6
64	8062	8069	8075	8082	8089	8096	8102	8109	8116	8122	1	1	2	3	3	4	5	5	6
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67	8261	8267	8274	8280	8287	8293	8299	8306	8312	8319	1	1	2	3	3	4	5	5	6
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69	8388	8395	8401	8407	8414	8420	8426	8432	8439	8445	1	1	2	2	3	4	4	5	6
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71	8513	8519	8525	8531	8537	8543	8549	8555	8561	8567	1	1	2	2	3	4	4	5	5
72	8573	8579	8585	8591	8597	8603	8609	8615	8621	8627	1	1	2	2	3	4	4	5	5
73	8633	8639	8645	8651	8657	8663	8669	8675	8681	8686	1	1	2	2	3	4	4	5	5
74	8692	8698	8704	8710	8716	8722	8727	8733	8739	8745	1	1	2	2	3	4	4	5	5
75	8751	8756	8762	8768	8774	8779	8785	8791	8797	8802	1	1	2	2	3	3	4	5	5
76	8808	8814	8820	8825	8831	8837	8842	8848	8854	8859	1	1	2	2	3	3	4	5	5
77	8865	8871	8876	8882	8887	8893	8899	8904	8910	8915	1	1	2	2	3	3	4	4	5
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79	8976	8982	8987	8993	8998	9004	9009	9015	9020	9026	1	1	2	2	3	3	4	4	5
80	9031	9036	9042	9047	9053	9058	9063	9069	9074	9079	1	1	2	2	3	3	4	4	5
81	9085	9090	9096	9101	9106	9112	9117	9122	9128	9133	1	1	2	2	3	3	4	4	5
82	9138	9143	9149	9154	9159	9165	9170	9175	9180	9186	1	1	2	2	3	3	4	4	5
83	9191	9196	9201	9206	9212	9217	9222	9227	9232	9238	1	1	2	2	3	3	4	4	5
84	9243	9248	9253	9258	9263	926[illegible]	9274	9279	9284	9289	1	1	2	2	3	3	4	4	5
85	9294	9299	9304	9309	9315	932[illegible]	9325	9330	9335	9340	1	1	2	2	3	3	4	4	5
86	9345	9350	9355	9360	9365	937[illegible]	9375	9380	9385	9390	1	1	2	2	3	3	4	4	5
87	9395	9400	9405	9410	9415	942[illegible]	9425	9430	9435	9440	0	1	1	2	2	3	3	4	4
88	9445	9450	9455	9460	9465	9469	9474	9479	9484	9489	0	1	1	2	2	3	3	4	4
89	9494	9499	9504	9509	9513	9518	9523	9528	9533	9538	0	1	1	2	2	3	3	4	4
90	9542	9547	9552	9557	9562	9566	9571	9576	9581	9586	0	1	1	2	2	3	3	4	4
91	9590	9595	9600	9605	9609	9614	9619	9624	9628	9633	0	1	1	2	2	3	3	4	4
92	9638	9643	9647	9652	9657	9661	9666	9671	9675	9680	0	1	1	2	2	3	3	4	4
93	9685	9689	9694	9699	9703	9708	9713	9717	9722	9727	0	1	1	2	2	3	3	4	4
94	9731	9736	9741	9745	9750	9754	[illegible]759	9763	9768	9773	0	1	1	2	2	3	3	4	4
95	9777	9782	9786	9791	9795	9800	[illegible]805	9809	9814	9818	0	1	1	2	2	3	3	4	4
96	9823	9827	9832	9836	9841	9845	[illegible]	9854	9859	9863	0	1	1	2	2	3	3	4	4
97	9868	9872	987[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]899	9903	9908	0	1	1	2	2	3	3	4	4
98	9912	9917	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	9948	9952	0	1	1	2	2	3	3	4	4
99	9956	996[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	9991	9996	0	1	1	2	2	3	3	3	4

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[illegible]772	9795	9817	9840	9863	9886	9908	9931	9954	9977	7 9 11 1 ... 20

Logarithms	0	1	2	3	4	5	6	7	8	9	Proportional Parts 1	2	3	4	5	6	7	8	9
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.01	1023	1026	1028	1030	1033	1035	1038	1040	1042	1045	0	0	1	1	1	1	2	2	2
.02	1047	1050	1052	1054	1057	1059	1062	1064	1067	1069	0	0	1	1	1	1	2	2	2
.03	1072	1074	1076	1079	1081	1084	1086	1089	1091	1094	0	0	1	1	1	1	2	2	2
.04	1096	1099	1102	1104	1107	1109	1112	1114	1117	1119	0	1	1	1	1	2	2	2	2
.05	1122	1125	1127	1130	1132	1135	1138	1140	1143	1146	0	1	1	1	1	2	2	2	2
.06	1148	1151	1153	1156	1159	1161	1164	1167	1169	1172	0	1	1	1	1	2	2	2	2
.07	1175	1178	1180	1183	1186	1189	1191	1194	1197	1199	0	1	1	1	1	2	2	2	2
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.12	1318	1321	1324	1327	1330	1334	1337	1340	1343	1346	0	1	1	1	2	2	2	2	3
.13	1349	1352	1355	1358	1361	1365	1368	1371	1374	1377	0	1	1	1	2	2	2	3	3
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.15	1413	1416	1419	1422	1426	1429	1432	1435	1439	1442	0	1	1	1	2	2	2	3	3
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.19	1549	1552	1556	1560	1563	1567	1570	1574	1578	1581	0	1	1	1	2	2	3	3	3
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.21	1622	1626	1629	1633	1637	1641	1644	1648	1652	1656	0	1	1	2	2	2	3	3	3
.22	1660	1663	1667	1671	1675	1679	1683	1687	1690	1694	0	1	1	2	2	2	3	3	3
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.24	1738	1742	1746	1750	1754	1758	1762	1766	1770	1774	0	1	1	2	2	2	3	3	4
.25	1778	1782	1786	1791	1795	1799	1803	1807	1811	1816	0	1	1	2	2	2	3	3	4
.26	1820	1824	1828	1832	1837	1841	1845	1849	1854	1858	0	1	1	2	2	3	3	3	4
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.29	1950	1954	1959	1963	1968	1972	1977	1982	1986	1991	0	1	1	2	2	3	3	4	4
.30	1995	2000	2004	2009	2014	2018	2023	2028	2032	2037	0	1	1	2	2	3	3	4	4
.31	2042	2046	2051	2056	2061	2065	2070	2075	2080	2084	0	1	1	2	2	3	3	4	4
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.41	2570	2576	2582	2588	2594	2600	2606	2612	2618	2624	1	1	2	2	3	4	4	5	5
.42	2630	2636	2642	2649	2655	2661	2667	2673	2679	2685	1	1	2	2	3	4	4	5	6
.43	2692	2698	2704	2710	2716	2723	27[illegible]	[illegible]	[illegible]	274[illegible]	[illegible]	[illegible]	2	3	3	4	4	5	6
.44	2754	2761	2767	2773	2780	2786	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	3	3	4	4	5	6
.45	2818	2825	2831	2838	2844	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	3	4	5	5	6
.46	2884	2891	2897	2904	291[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	4	5	5	6
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.48	3020	3027	3034	30[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	5	6	6
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Logarithms	0	1	2	3	4	5	6	7	8	9	Proportional Parts 1	2	3	4	5	6	7	8	9
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.52	3311	3319	3327	3334	3342	3350	3357	3365	3373	3381	1	2	2	3	4	5	5	6	7
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.59	3890	3899	3908	3917	3926	3936	3945	3954	3963	3972	1	2	3	4	5	5	6	7	8
.60	3981	3990	3999	4009	4018	4027	4036	4046	4055	4064	1	2	3	4	5	6	6	7	8
.61	4074	4083	4093	4102	4111	4121	4130	4140	4150	4159	1	2	3	4	5	6	7	8	9
.62	4169	4178	4188	4198	4207	4217	4227	4236	4246	4256	1	2	3	4	5	6	7	8	9
.63	4266	4276	4285	4295	4305	4315	4325	4335	4345	4355	1	2	3	4	5	6	7	8	9
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.83	6761	6776	6792	6808	6823	6839	6855	6871	6887	6902	2	3	5	6	8	9	11	13	14
.84	6918	6934	6950	6966	6982	6998	7015	7031	7047	7063	2	3	5	6	8	10	11	13	15
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.86	7244	7261	7278	7295	7311	7328	7345	7362	7379	7396	2	3	5	7	8	10	12	13	15
.87	7413	7430	7447	7464	7482	7499	7516	7534	7551	7568	2	3	5	7	9	10	12	14	16
.88	7586	7603	7621	7638	7656	7674	7691	7709	7727	7745	2	4	5	7	9	11	12	14	16
.89	7762	7780	7798	7816	7834	7852	7870	7889	7907	7925	2	4	5	7	9	11	13	14	16
.90	7943	7962	7980	7998	8017	8035	8054	8072	8091	8110	2	4	6	7	9	11	13	15	17
.91	8128	8147	8166	8185	8204	8222	8241	8260	8279	8299	2	4	6	8	9	11	13	15	17
.92	8318	8337	8356	8375	8395	8414	8433	8453	8472	8492	2	4	6	8	10	12	14	15	17
.93	8511	8531	8551	8570	8590	8610	8630	8650	8670	8690	2	4	6	8	10	12	14	16	18
.94	8710	8730	8750	8770	8790	8810	8831	8851	8872	8892	2	4	6	8	10	12	14	16	18
.95	8913	8933	8954	8974	8995	9016	9036	9057	9078	9099	2	4	6	8	10	12	15	17	19
.96	9120	9141	9162	9183	9204	9226	9247	9268	9290	9311	2	4	6	8	11	13	15	17	19
.97	9333	9354	9376	9397	9419	9441	9462	9484	9506	9528	2	4	7	9	11	13	15	17	20
.98	9550	9572	9594	9616	9638	9661	9683	9705	9727	9750	2	4	7	9	11	13	16	18	20
.99	9772	9795	9817	9840	9863	9886	9908	9931	9954	9977	2	5	7	9	11	14	16	18	20

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